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FLOCCULANTS

SUMMARY REPORT

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July 18, 1980

TO:

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SUBJECT:

SUMMARY REPORT, MARCH, 1980
COVERING WORK CONDUCTED AT
RAYLO CHEMICALS LIMITED BY
DRS. R. VUKOV AND F. SKINNER

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ABSTRACT

A total of 95 commercial flocculants and several commercial polymer standards have been chemically characterized using spectroscopic and wet chemical techniques adapted for this purpose by Raylo Chemicals, and were found to be either anionic, cationic, or neutral polyacrylamides, cationic polyamines, or anionic sodium polyacrylates. The degree of ionic functionalization was determined for all flocculants. The sensitivity of the most numerous type, anionic polyacrylamide, to degradation by physical and chemical conditions likely to be encountered by these flocculants was investigated using a small number of samples. Finally, small amounts of anionic, neutral and cationic polymers were prepared for use as standards for analyses and for investigation of the stereochemical structure of polyacrylamide.

INTRODUCTION

Flocculants are widely used for the removal of suspended fine particulates from different aqueous effluents. Several hundred flocculants from over 30 suppliers are presently sold commercially in Canada. Of these, approximately 100 have been recommended by suppliers for use in coal operations. In spite of this abundance, difficulties occur in achieving satisfactory performance of flocculants under industrial conditions. This is in part attributable to a continual change in the conditions that can affect flocculant performance. The chemical characterization of flocculants and the correlation of these characteristics with performance under different conditions would therefore be of great assistance in preparing effective water treatment techniques.

The objective of this study was to characterize commercially available flocculants. The work, as laid out in the Statement of Work in the original contract and modified in discussions with the Scientific Authority, Dr. H.A. Hamza, of Western Regional Laboratories, was to proceed in three overlapping phases.

Phase I of the project involved the development of new analytical techniques, and subsequent analysis of commercial flocculants by the newly developed wet chemical and spectroscopic techniques. Primarily,

the assignment of a flocculant to either an anionic, neutral, or cationic classification and a quantitative value for its activity had to be determined. In addition, the chemical functionalities present in the flocculant were of importance. The detection and identification of inorganic salts found in certain organic flocculant samples was also of some importance. Finally, the analysis of the molecular weight of certain flocculants was considered essential.

Phase II of the project involved the correlation of probable flocculant performance with the chemical characteristics of the flocculants determined in the initial phase of the study. Due to the large number of variables to be considered in evaluating probable flocculant performance, including the effects of different ions, dissolved gases, and other conditions that could affect the performance of each sample under investigation, only a limited number of flocculants chemically characterized in Phase I were to be so investigated.

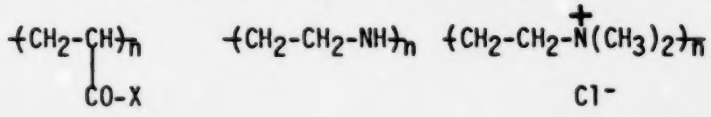
Phase III of the project involved the preparation of small amounts of polymers by either complete synthesis from the monomeric precursor or by post-modification of a well characterized commercial sample. The initial aim of this undertaking was to prepare samples containing known functionalities in order to obtain standards for the various analytical methods developed in Phase I of the project, as very few commercial standards exist. The possibility of preparing small samples of

specially tailored flocculants of presumably superior performance was envisaged, but insufficient time was available.

RESULTS AND DISCUSSION

I. CHEMICAL CHARACTERIZATION OF COMMERCIAL FLOCCULANTS

The commercial flocculants selected for analysis by the Scientific Authority, Dr. H.A. Hamza, were usually identified only by a sample number. The flocculants were reported to include neutral compounds such as polyacrylamide 1, anionic polyelectrolytes such as



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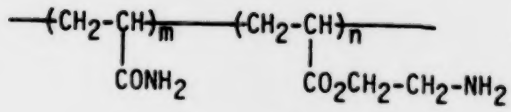
1 x = NH_2

2 x = NH_2 or O^-Na^+

partially hydrolyzed polyacrylamide 2, and cationic polymers such as polyethyleneimine 3, or similar products with quaternized ammonium functionalities 4. Other possible cationic flocculants may be based on polyaminoalkyl acrylates, such as the cationic polymer 5.



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The determination of the nature and abundance of the different functionalities was carried out by a combination of spectroscopic and wet chemical methods.

1. Spectroscopic Analysis

a) Infrared Spectroscopy:

Infrared spectroscopic analysis of casts of flocculant solutions on silver chloride plates represented an excellent method for the determination of common functionalities in a polymer. Thus, the vast majority of samples could immediately be assigned to the most common chemical classes of flocculant, either neutral polyacrylamide, characterized by absorptions at 3400 - 3200 cm^{-1} (see Figure 1), partially hydrolyzed and therefore anionic polyacrylamide, characterized by additional absorptions at 1550 and 1400 cm^{-1} (see Figure 2), cationic polyacrylamide, characterized by additional absorptions at 1740, 1440 and 950 cm^{-1} (see Figure 3), or cationic polyamines, characterized by absorptions at 1650 and 1150 cm^{-1} (see Table 1 for a listing of key absorptions).

Spectra were recorded on three different infrared spectrophotometers. The spectra were routinely obtained on a Perkin Elmer 137

infrared spectrophotometer. In addition, numerous samples were analyzed with a Perkin Elmer 283 infrared spectrophotometer through the co-operation of the Western Regional Laboratories of the Energy Research Laboratories. The slight improvement in resolution obtained by use of the Fourier Transform infrared spectrophotometer available at the University of Alberta was not significant.

The relative intensity of the 1550 and the 1400 cm^{-1} absorption in comparison to the 1650 cm^{-1} absorption of anionic polyacrylamides was found to give a qualitative measure of the degree of hydrolysis of the polyacrylamide. This enabled a large number of anionic polyacrylamides to be arranged in order of increasing degree of hydrolysis, an ordering largely confirmed by wet chemical techniques. Attempts to develop a quantitative method for the determination of the degree of hydrolysis by this method were partially successful, with an absolute error of 5% or more between the infrared-derived and the more reliable wet chemical method results.

The commercial method for the synthesis of the monomer acrylamide has, until recently, been carried out by the treatment of acrylonitrile with sulphuric acid, and subsequent neutralization and purification of the product (1). In many polyacrylamide flocculants however, substantial amounts of sodium or ammonium sulphate are present, attributable to inadequate purification of the monomer, or deliberate addition of inorganic salt, presumably to assist in rapid flocculant

dissolution (2). The presence of substantial amounts of sulphate anion in the flocculant can be investigated by infrared spectroscopy, as the anion has a strong absorption near 1120 cm^{-1}. Attempts to develop a quantitative analytical technique based on this method were only marginally successful (see Experimental). However the detection of the sulphate absorption remains a useful qualitative indication of the presence of inorganic salt, which can then be investigated by wet chemical techniques. Thus, the strong absorption at 1120 cm^{-1} in Figure 1 was found to correspond to 45.8% sodium sulphate by weight.

Another absorption found in the spectra of a substantial number of the polyacrylamide-based flocculants was located at 1730 cm^{-1}, attributable to an ester functionality. The majority of the cationic polyacrylamide based flocculants exhibited this absorption, suggesting the presence of an aminoalkyl acrylate copolymer such as that illustrated above in structure 5. In the case of anionic polyacrylamides this absorption could arise from the use of methyl acrylate 6 as a termonomer. In the anionic flocculant samples

$$CH_2=CH-CO_2CH_3$$

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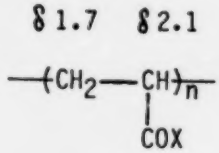
exhibiting this absorption, resonances near 3.5 were observed in the nuclear magnetic resonance spectra suggestive of a methyl ester.

b) Nuclear Magnetic Resonance Spectroscopy:

The analysis of dried flocculant samples by proton magnetic resonance spectroscopy using deuterium oxide as solvent has been carried out for all samples received. In addition, the solubility of a few cationic flocculant samples in dimethylsulphoxide-d_6 allowed substitution of this solvent for deuterium oxide. The samples were routinely analyzed on a Varian EM-60 proton magnetic spectrophotometer. Fourier transform carbon-13 and high resolution proton magnetic resonance spectra were obtained using facilities at the University of Alberta.

The low resolution proton magnetic resonance spectra of the flocculants fell into three classes (see Table 2 for characteristic resonances). The first, containing the majority of the flocculants, showed broad resonances near δ1.7 and δ2.1, as illustrated in Figure 5, attributable to the methylene and methine protons respectively of the backbone of a polyacrylamide-based polymer. All flocculants in this



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class were found to be anionic or neutral flocculants by wet chemical methods.

The second class contained spectra that closely resembled those in the first class, but in addition contained resonances between δ 3.0 and δ4.0. Flocculants later determined to be anionic in nature usually exhibited a single resonance near δ3.7, suggestive of a methylacrylate copolymer, as discussed earlier. Those later found to be cationic polyacrylamide-based flocculants exhibited some differences in detail, but usually contained a sharp singlet near δ3.2, characteristic of a methyl group adjacent to a quaternary nitrogen (see Figure 6 for example). The integral of this resonance in comparison to that of the backbone protons of the polyacrylamide yielded a qualitative indication of the degree of cationic functionalization of the polyacrylamide-based flocculant.

The third class of spectra contained substantial resonances only between δ3.0 and δ3.6, indicative of the presence of quaternary or protonated amines (see Figure 7 for example). All these flocculants were later found to be cationic in nature.

Low resolution proton magnetic resonance spectroscopy represents a useful tool for assisting in the rapid classification of flocculants, allowing rapid confirmation of the identification of flocculants as neutral, anionic, or cationic polyacrylamides. The elucidation of the complete structure of cationic functionalities is not yet possible using spectral methods, but as well characterized standards are obtained from different sources, more complete characterization will be possible.

The direct determination of the degree of hydrolysis of anionic polyacrylamide flocculants by integration of their Fourier transform carbon-13 magnetic resonance spectra investigated, and found to be feasible. In the carbon-13 spectrum of a partially hydrolyzed polyacrylamide (see Figure 8 for example), two downfield resonances near 180 ppm can be seen. Assignment of the resonance near 184 ppm to the carboxylate functionality, and that near 180 ppm to the amide functionality (3), and integration of these resonances, as shown in Figure 9, yielded a degree of hydrolysis within 5% of the value determined by wet chemical methods, as noted in Table 3. Due to the low concentration of carbon-13 in organic materials (1.1%) and the low flocculant concentration required to give solutions of low viscosity (2%), the spectra were unable to show the carbonyls of carboxylate functionalities present in less than 5% of the total carbonyl content even after 6 hours of data accumulation. This value of 5% therefore represents both a lower limit for the detectable degree of hydrolysis, and the typical deviation between the spectroscopic and conductometric results. The technique will be employed in the future to characterize anionic flocculants which yield unsatisfactory results by the normal wet chemical analytical methods.

c) Ultraviolet Spectroscopy:

Ultraviolet spectroscopy represents both the least useful and the potentially most sensitive spectroscopic technique for the analysis of flocculants. This apparent contradiction is due to the chemical make-up of the vast majority of flocculants - they contain no useful ultraviolet chromophore. Should a small amount of a typical chromophore such as a phenyl group be present, however, the easily detected ultraviolet band may be the only indication of the functionality, as its low concentration makes it difficult to detect by other spectroscopic methods.

Thirteen of the ninety-five commercial flocculants exhibited some ultraviolet bands, of which seven had bands solely in the region from 255 nm to 265 nm, suggesting an aromatic chromophore. The absorbtivity of these samples was low, varying between 4 and 40, in comparison to values of 215 and 2750 for benzene and pyridine (4), the most probable aromatic chromophores. This and the absence of all aromatic resonances in the nuclear magnetic resonance spectra of these samples indicated that the suspected aromatic functionalities were under 5% by weight. Other flocculants showed bands from 219 nm to 314 nm, with a similar range in absorbtivities. Here again, no spectral features attributable to the more common ultraviolet chromophores were visible in the infrared or nuclear magnetic resonance spectroscopy of these samples, indicating that only a small amount of the chromophore was present.

The low number of flocculants that contain ultraviolet chromophores and the low concentration of the chromophores in those cases suggested that their presence was not significant, therefore little effort to elucidate the nature of the chromophore was made. Should flocculation experiments carried out at the Western Regional Laboratories indicate any difference between these samples and other chemically similar samples that lack ultraviolet chromophores, analyses to determine the exact functionality will be carried out.

2) Wet Chemical Analysis

a) Physical Analysis:

The physical nature of the flocculants, either solid or liquid, was noted, and the content of volatiles determined by warming a sample in a vacuum oven. A clear correlation between the type of polymer and the sample's physical state was noted. Thus over 80% of the polyacrylamide and polyacrylic acid-based flocculants were solids, whether the sample was cationic, anionic or neutral in make-up. Similarly over 80% of the polyamine-based flocculants, all cationic, were liquids or suspensions.

The volatile content of the flocculants was used in all calculations to get the volatile free content of functionalities.

b) Potentiometric and pH Titrations:

Solutions of anionic and neutral flocculants were routinely titrated with sodium hydroxide after acidification by either direct addition of acid or passage of the flocculant solution down a cation exchange resin column (see Figure 10 for an example of such a titration). The end-point of the titration, that is, the point of steepest slope, marks the point at which all of the strong, and weak acids have been neutralized, as in equation 1.

$$\text{Polymer-}CO_2H \xrightarrow{NaOH} \text{Polymer-}CO_2^-Na^+ \quad (1)$$

The separate determination of the added strong acid and the weak acid due to the partially hydrolyzed polyacrylamide flocculant was however not possible by pH titration. Attempts to carry out separate determinations of strong and weak acid by potentiometric titration were also unsuccessful (5). Conductometric titration was therefore employed for this purpose.

c) Conductometric Titration:

Conductometry measures the total conductance of all of the ions in a solution (6). At both the start and the end of an acid-base conductometric titration, the solution conductance will be high, due to the presence of a high concentration of hydrogen or hydroxide ions respectively. Between these extremes, the solution conductance

initially drops steadily to a minimum at which point all of the strong acid has been neutralized (see Figure 10). Further addition of base causes a slow rise in conductance, characteristic of the presence of both weak acids or weak bases. Finally, a rapid rise in conductance on continued addition of base marks the end-point of the titration of the weak acids and bases.

In practice, the carboxylic acid content of the flocculant and hence the degree of hydrolysis of the polyacrylamide could normally be calculated from the base added during the slow rise in solution conductance (see Experimental). Occasionally, the end-point of the pH titration and the second end-point of the conductometric titration were substantially different, as shown in Figure 10. This was later found to be attributable to the presence of the inorganic ammonium cation instead of the more usual sodium cation, requiring additional base to neutralize all weakly ionic species (see equation 2).

$$\text{Polymer-}CO_2H + NH_4^+ \xrightarrow{NaOH} \underset{\text{(pH endpoint)}}{\text{Polymer-}CO_2^- Na^+} + NH_4^+$$

$$\xrightarrow{NaOH} \underset{\text{(conductometric endpoint)}}{\text{Polymer-}CO_2^- Na^+} + NH_3 \qquad (2)$$

Flocculant solutions that had been passed down cation exchange columns never exhibited this effect. As all cations were converted to hydrogen ions by this treatment, as shown in equation 3, the pH and

$$\text{Polymer}\begin{vmatrix}-CO_2^-Na^+\\-CO_2^-NH_4^+\end{vmatrix} \xrightarrow[\text{exchange}]{\text{cation}} \text{Polymer}\begin{vmatrix}-CO_2H\\-CO_2H\end{vmatrix} \quad (3)$$

second conductometric end-points should and did appear coincident. Therefore conductometric titrations were usually carried out on flocculant samples thus treated.

Treatment of the polymer sample in this manner has an additional benefit - neutral inorganic salts such as sodium sulphate, normally undetectable by pH and conductometric titration, are converted into a strong acid such as sulphuric acid (see equation 4). The quantity of

$$\text{Polymer-N}CO_2^-Na^+ + Na_2SO_4 \xrightarrow[\text{exchange}]{\text{cation}} \text{Polymer-}CO_2H + H_2SO_4 \quad (4)$$

acid produced by cation exchange can be easily measured by pH or conductometric titration, allowing rapid determination of the inorganic salt content of the flocculant. The identity of the salt is usually sodium sulphate (2), as was usually confirmed by inspection of the infrared spectrum. In the few cases that substantial salt was present,

yet no sulphate infrared absorption was evident, an unknown inorganic salt is indicated. No effort to determine the anion has yet been made in these cases.

d) Colloid Titration:

The mixing of a cationic and an anionic polyelectrolyte leads to the formation of a complex whose composition, although sensitive to many variables, tends towards a stoichiometric reaction between the oppositely charged functionalities on the polymers (see Diagram 1). Polyelectrolyte solutions have been titrated quantitatively with known

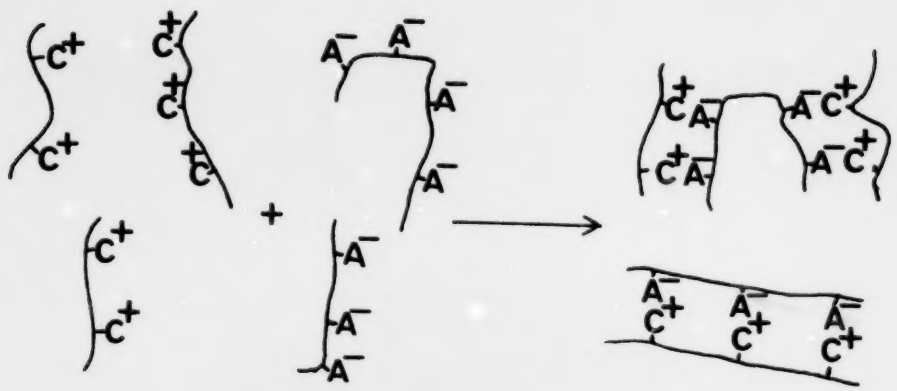
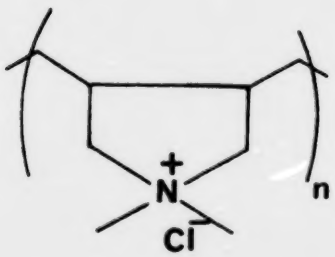


Diagram 1. Complexation of Cationic and Anionic Polyelectrolytes.

concentrations of oppositely charged polymers either colorimetrically (7) or conductometrically (8). After some experimentation, a satisfactory method of colloid titration, involving the addition of a

addition of a known amount of the cationic polymer polydiallyldimethylammonium chloride 8 to the unknown sample, and subsequent titration of the mixture with potassium polyvinylsulphate 9 was developed. Titrations were carried out in duplicate and showed good reproducibility. Both cationic and anionic samples can be



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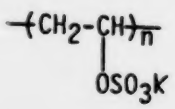

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evaluated with this technique, the former being characterized by titration volumes above that required for a blank, and the latter by results less than that found for a blank sample (see Experimental for procedure).

Results obtained for anionic flocculants were used to calculate an expected degree of hydrolysis, and this value was found to be about 40% higher than the extent of hydrolysis determined by conductometric titration. This discrepancy is believed to be a systematic error inherent in the colloid titration technique, possibly due to an impurity in the potassium polyvinylsulfate.

The results obtained for cationic flocculants were used to calculate the milliequivalents of cationic functionality per gram of sample, a common measure of ionic strength. These values, corrected for the systematic error, are noted in Tables 4 and 5.

Approximately half of the cationic flocculants were analyzed by conductometric titration, in an analogous manner to that used for anionic flocculants. This procedure by itself is of little use, as it measures only the weakly cationic functionalities such as amines, and cannot detect strongly ionic functionalities such as quaternary ammonium functionalities. However, in conjunction with the results of colloid titration, both the quantity and the nature of the active functional groups, whether strongly cationic, weakly cationic, or amphoteric, can be determined. Thus, a flocculant containing a large number of strongly cationic groups should give a high value in colloid titration, but be undetected by conductometric titration. A weakly cationic flocculant should yield similar values in both methods of titration. Finally, an amphoteric flocculant would yield a higher value by conductometric titration, which measures the total weakly ionic groups present, whether anionic or cationic, than by colloid titration, which determines the excess of cationic over anionic groups. This is noted in Tables 4 and 5.

Colloid titration represents the best method presently available to determine the strength of cationic flocculants, and in conjunction

with conductometric titration, can be used to examine the nature of the cationic functional groups. The technique can be used to examine anionic polymers, yielding results that show a consistent deviation from those determined by conductometric titration.

e) Kjeldahl Nitrogen Determination:

The determination of the weight percent of nitrogen in the majority of the flocculants received was carried out using the Kjeldahl nitrogen determination method. At the present time, only the results for anionic flocculants can be compared to properties determined by other methods. Thus as the degree of hydrolysis increased for different partially hydrolyzed polyacrylamide flocculants, the nitrogen content decreased as expected (see Table 6).

In general, the nitrogen content of polyacrylamides should be close to or somewhat below the calculated value. The reason why polyacrylamides often exhibit a lower nitrogen content than that calculated is due to the presence of a small amount of the imide group 10 in almost all samples of the polymer.

Polymer-CO-NH-CO-polymer

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Certain anionic polymers contained substantially more nitrogen than had been calculated. These were examined using volumetric

analysis (9) and ammonium cation was detected in about 20% of the anionic polyacrylamide flocculants. The source of this ammonium cation is uncertain as it could be derived from impurities remaining in the acrylamide monomer (1), or could be due to the deliberate addition of ammonium sulphate to assist the dissolution of the flocculant in water. Thus in one sample, ammonium was the only cation detected, strong evidence that its presence was deliberate, whereas in the remainder of ammonium-containing flocculants, the low preparation of ammonium to sodium cations suggested that impurities were responsible.

f) Cation Analysis by the Sodium Sensitive Electrode and Atomic Absorption Spectroscopy:

Solutions of the majority of flocculants received were analyzed by use of an Orion sodium sensitive electrode. The experimental sodium content of the anionic samples was compared to the expected value calculated from the conductometrically determined degree of hydrolysis and inorganic salt content on the assumption that sodium was the sole cation. The majority of samples showed satisfactory agreement, however a substantial minority showed a deficiency in the amount of sodium detected using the electrode. Most of these samples were found to contain the ammonium cation, as discussed previously, in amounts sufficient to explain the discrepancy.

In order to examine for other possible cations that may have been present in polyacrylamide, a number of anionic flocculants were analyzed for potassium magnesium and calcium by qualitative colorimetric methods, and a total of 20 flocculants examined further by atomic absorption spectroscopy. In no case was any calcium or magnesium detected. Potassium was found to be the major cation in one partially hydrolyzed polyacrylamide, sample 21, and to make up a fifth of the cation content of another, sample 29. Finally, potassium was the only cation detected in the partially hydrolyzed polyacrylamide sample 78.

g) Chemical Determination of the Amide Content of Polyacrylamide:

An analytical procedure obtained from Dow Chemical Company for the determination of the amide content of aqueous solutions (10) has given results for polyacrylamide flocculant solutions that show some correlation with the degree of hydrolysis as found by conductometric titration. This procedure is based on the oxidation of amides to N-bromoamides by bromine, as shown in Reaction 5. After removal of excess bromine, the N-bromoamide in turn is used to oxidize potassium

$$RCONH_2 \xrightarrow{Br_2} RCONHBr + HBr \qquad (5)$$

iodid to potassium triiodide, which can be quantitatively determined by measuring its absorbance at 287 nanometers (see Reaction 6). The

accuracy of the amide determination is therefore dependent on the complete reaction of the intermediates at each stage of the procedure.

$$RCONHBr + H^+ + 3I^- \longrightarrow RCONH_2 + Br^- + I_3^- \quad (6)$$

In practice, flocculants known to be unhydrolyzed polyacrylamides yielded results between 83 and 119% of the expected values. Furthermore, analyses of partially hydrolyzed polyacrylamides yielded consistently low results for the amide content by this method. Finally, cationic polyacrylamide flocculants yielded results indicating a far lower amide content than would be expected by analysis of the infrared spectrum. Although a tentative method for correction of the results of anionic polymers was developed, the high variability of the determined degree of hydrolysis, varying by up to 15% from the conductometrically determined value, rendered the analytical method of marginal value.

h) Molecular Weight Determinations:

Three methods for the determination of molecular weight are extensively used. The simplest (11, 12) involves determination of the intrinsic viscosity $[\eta]$, of the polymer in question and calculation of the molecular weight using the Mark-Houwink relationship:

$$[\eta] = KM^a$$

The variables "K" and "a" have previously been found for polyacrylamide by analysis of low molecular weight polymers of well-defined molecular weight. Although this method is rapid, the molecular weight distribution cannot be determined, and in addition, use of Mark-Houwink constants for polymers much larger than those used to determine these constants may introduce errors. Finally, only non ionic polymers can be investigated by this means, as ionic polymer molecules have poorly defined intrinsic viscosities.

The second method commonly used for the determination of polymer molecular weights involves separation of a sample into fractions of differing molecular weight by use of gel permeation chromatography (13, 14). The injection of polymers of known molecular weight allows the preparation of a calibration curve of retention volume versus molecular weight. Unfortunately, the poor reliability of the molecular weight data for the available polyacrylamide standards rendered this method of doubtful value.

The third method of molecular weight determination for high polymers is the analysis of the light scattering properties of polymer solutions (15, 16). All matter scatters light to some degree. A polymer solution, however, will scatter far more light than the solvent alone. Measurement of the magnitude of this scattering and knowledge of certain physical properties of the polymer can give an accurate determination of the weight average molecular weight of the polymer.

This method therefore allows the absolute determination of molecular weights without reference to standard polymers.

The molecular weight of all of the neutral flocculants was determined by intrinsic viscosity using a Cannon-Fenske viscometer of a type recommended by Dr. Hamielec (see Table 10). In addition, several neutral flocculants were examined by gel permeation chromatography, using a Waters Model 6000A Solvent Delivery System, five 4 foot columns packed with Controlled Pore Glass, and a Waters R401 Differential Refractometer Detector. The molecular weights and molecular weight distributions determined using this method must, however, remain suspect until confirmed by light scattering analysis. The Chromatix KMX-6 Low Angle Laser Light Scattering Photometer has been delivered and will commence such analyses shortly.

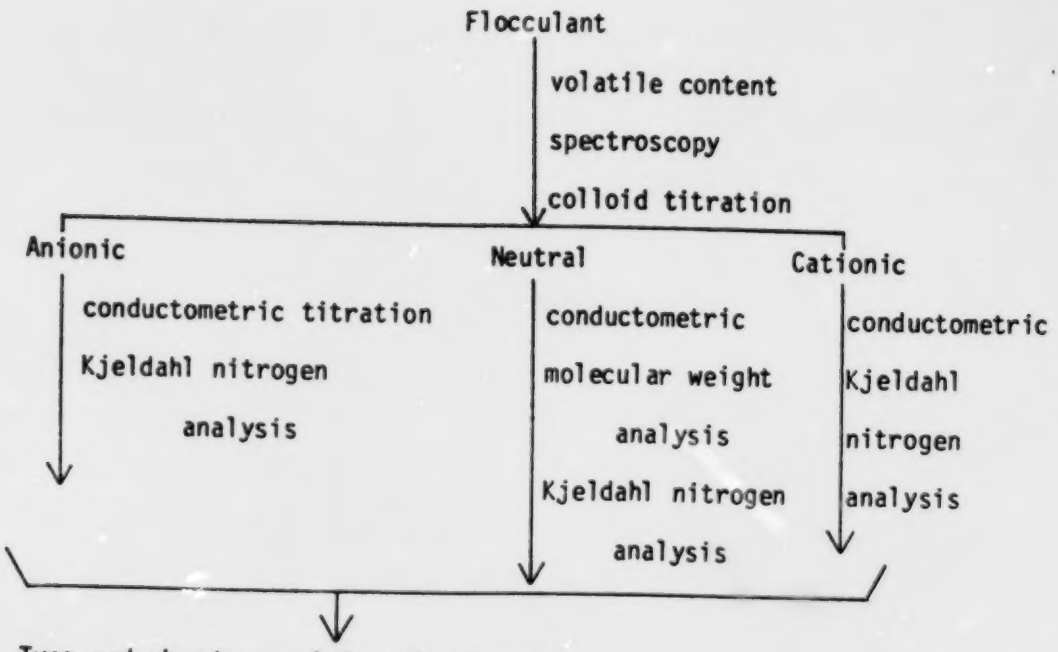
3. Results of Chemical Analysis of Flocculants

A total of 95 commercial flocculant samples identified only by number, and chosen by Dr. Hamza of Energy, Mines and Resources to represent a range of flocculant types and manufacturers, were analyzed. In addition several named samples of flocculants and polymers, largely obtained from Energy, Mines and Resources, were examined. These will be discussed below. Analyses carried out on synthesized polymers will be discussed later.

a) Analysis of numbered flocculant samples:

Each flocculant sample received was subjected to initial testing to determine the nature of the flocculant, either anionic, neutral, or cationic, and subsequent tests determined with this knowledge. An

Scheme 1

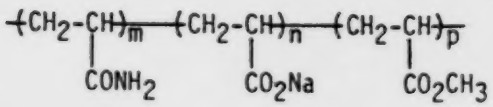


outline is shown in Scheme 1. In addition, all flocculants were analyzed for sodium using the sodium sensitive electrode, and selected flocculants tested for calcium, magnesium and ammonium cations by

atomic absorption spectroscopy and other means.

The 95 samples fell into three groups, anionic, neutral and cationic. A total of 54 anionic flocculants were examined and the majority found to be partially hydrolyzed polyacrylamides with degrees of hydrolysis up to about 65% (see Table 6). Two anionic samples, however, were partially neutralized polyacrylic acid. These flocculants, samples 11 and 73, could be derived from hydrolyzed polyacrylonitrile, neutralized polyacrylic acid, or acidified sodium polyacrylate.

The majority of the anionic polyacrylamide flocculants showed no evidence of functionalities other than amide and carboxylate. Three flocculants, samples 17, 27 and 32 contained small amounts of ester functionality, indicating that their structure resembled the terpolymer 11.



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A total of 10 neutral and anionic flocculants were found to contain greater than 7% by weight of inorganic salt (see Tables 6 and 7). The majority of these, samples 4, 30, 34, 41, 50, 55 and 67 also exhibited substantial infrared absorptions attributable to the sulphate anion, while a minority, samples 15, 28 and 76, contained as yet

unidentified salt assumed to be sodium chloride.

Substantial amounts of ammonium cation, greater than about 0.25% by weight, were found in 15 anionic flocculants, as noted in Table 8, but only in sample 27 was it the only cation detected. In the other samples, it made up less than half of all the cations present, suggesting its presence may be attributable to impurities in the monomer acrylamide.

Potassium made up most of the cations in samples 21 and 78, about half in sample 67, and approximately a fifth of those in sample 29. No cations other than sodium, ammonium or potassium were detected in any anionic flocculant.

A total of 7 neutral flocculants, all polyacrylamides, were characterized as usual and the results are noted in Table 7. The molecular weights of several neutral polyacrylamide flocculants are noted in Table 9. The variation in the results obtained by different methods is expected to be resolved once the Chromatix Low Angle Laser Light Scattering Photometer is fully operational. The other analytical results were discussed with those of the anionic flocculants.

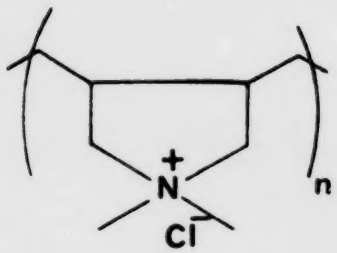
A total of 34 flocculants were found to be cationic in nature. Of these, 22 were determined by spectroscopic analysis to be polyacrylamide-based polymers, and the remaining 12 to be polyamine, usually quaternized (see Tables 4 and 5). Kjeldahl analysis yielded the nitrogen content of these flocculants, and allowed division of the cationic samples into two groups, the first of which exhibited a

nitrogen content of 10% and above, and yet had a low cationic content. These flocculants were all polyacrylamide-based. The second group, characterized by a substantially higher cationic content and a much lower nitrogen content contained all of the polyamine flocculants. The Kjeldahl nitrogen determination therefore assisted in the classification of cationic flocculants, and allowed a rough estimation of the degree of cationic functionalization of the flocculant.

b) Analysis of additional polymer samples:

A number of polymer standards were received from Energy, Mines and Resources Laboratories or direct from the manufacturer. The majority of these samples were described as and found to be partially hydrolyzed polyacrylamide (see Table 10). One such sample, reported to be 24.7% hydrolyzed by Dr. A.E. Hamielec, yielded the correct result by conductometry. In addition two named polymers, Polyhall 402 and Alchem flocculant 5WJ682, were received from Dr. H. Hamza. Polyhall 402 was found to be a neutral polyacrylamide, whereas the Alchem sample consisted of a white suspension in an organic liquid and a solution of "activator" supplied in a separate container. The suspended material was found to be sodium polyacrylate, and the activator was identified as polyethylene oxide containing aromatic end groups.

Finally, a sample of a cationic polymer, polydiallyldimethyl-ammonium chloride 8 was analyzed spectroscopically and found to have nearly identical infrared and nuclear magnetic spectral characteristics



8

to samples 14, 56, 57 and 89. All four flocculants indeed had a nitrogen content of about 8%, close to the expected value of 8.6%.

Further analysis of characterized polymers will continue in order to assist in the identification of flocculants.

II. DEGRADATION OF POLYACRYLAMIDES BY PHYSICAL & CHEMICAL MEANS

The ability of a flocculant molecule to coagulate suspended particles into easily seperable floccs is strongly dependent on the polymer's molecular weight, larger molecules being most efficient. Degradation of the polymeric molecule would therefore decrease its flocculating ability.

The degradation of polyacrylamide both by harsh mechanical treatment such as high speed stirring or ultrasonic radiation (17) and by strong chemical treatment such as oxidation with ozone (18) are well documented. These extreme conditions would not be encountered in normal flocculation conditions, however, so the effects of much milder degradation treatment were investigated.

Solutions of four anionic polyacrylamides ranging in degree of hydrolysis from 0 to 39.6% were slowly stirred for extended periods of time, and changes in the viscosity of each solution observed. In all cases, the viscosity of the solutions rose rapidly for some time after the flocculant was added to the water, and then slowly decreased. The initial increase, attributable to the dissolution of the flocculant, took between 30 minutes for the most hydrolyzed polyacrylamide up to about four hours for the unhydrolyzed polyacrylamide flocculants. The subsequent decrease in viscosity was followed for two weeks, and never exceeded 50% for any flocculant, averaging about 25%. While these values are much too crude to calculate any decrease in molecular weight, the final molecular weight must have been at least half the initial value, indicating that little change could be attributable to air oxidation of the polymer.

The majority of ionic species likely to be encountered in systems requiring flocculation are not chemically reactive, however the ferric ion, a likely constituent of mine washings, has been used as an oxidant for organic molecules (19). The stability of four partially hydrolyzed polyacrylamide based flocculants was measured over time in distilled water and 30 ppm ferric ion both with and without exposure to air. The presence or absence of air caused little change in the average drop in viscosity over time. On the other hand the presence of 30 ppm ferric ion caused a slower decrease in viscosity over time for all the

flocculants except the non-hydrolyzed sample. This indicates that ferric ion prevents the apparent slow degradation of partially hydrolyzed polyacrylamides.

This may be attributable to the effects of the ionic solution on the conformation of the polymer molecule. In a solution of low ionic strength, each polymer molecule will extend itself due to the electrostatic repulsion of the anionic groups on the polymer backbone as shown in Diagram 2a.

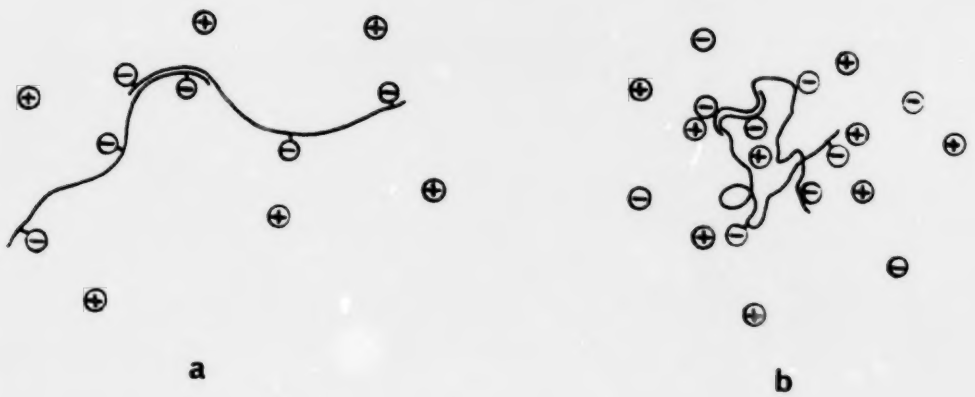


Diagram 2. Polyelectrolyte in salt-free and ionic solutions.

In an ionic solution, the high content of cations co-ordinate with and effectively nullify the polymers anionic groups, allowing the polymer chain to relax into a random coil, as illustrated in Diagram

2b. This much smaller random coil, aside from yielding a much lower solution viscosity, may be less sensitive to degradative forces.

The effect of the identity of the cation on the conformation of the flocculant was also investigated. The relative viscosity of four flocculants in solutions containing varying amounts of sodium, magnesium, cupric and ferric ion was measured, and the results for one of the flocculants are shown in Figure 11. None of the flocculants investigated would dissolve in or remain in solution in the more concentrated ferric nitrate solutions, so the viscosity versus ion concentration for this ion is merely an estimate based on one reading.

As illustrated in Figure 11, the viscosity of the polymer decreased as ionic strength increased until a minimum value was achieved. The sensitivity of the polymer to different salts varied substantially however, with monovalent sodium causing a small shift at any ion concentration. Divalent magnesium was about three times as effective at reducing viscosity, while cupric and ferric salts, distinguished by the transition metals ability to co-ordinate strongly to the carboxylate functionalities of the backbone, reduced the polymer solutions's viscosity to its minimum value at less than a tenth of the cation concentration required for sodium chloride. Investigation of the effects of low concentrations of transition metals on the flocculating properties of ionic polymers may therefore be useful.

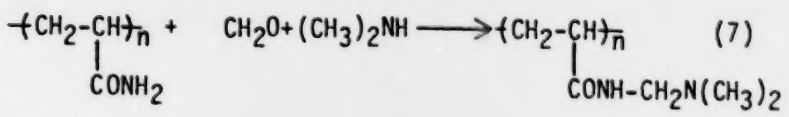
III. SYNTHESIS AND CHARACTERIZATION OF REPRESENTATIVE POLYMERS

As discussed in the Introduction, two methods for the preparation of new polymers exist, the first being chemical post-modification of available commercial polymers, and the second being complete synthesis from monomers. Both methods were used extensively.

1) Post-modification of Polymers

a) Preparation of cationic polyacrylamides via the Mannich reaction:

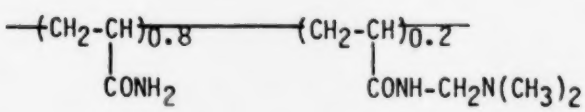
The introduction of a cationic functionality such as an amine or quaternary amine is required in order to convert a neutral polyacrylamide to a cationic polymer. Use of polyacrylamide as the starting material for the Mannich reaction would yield a tertiary amine containing polymer, as shown in equation 7.



(7)

Initial attempts to modify polyacrylamide using the commonly accepted acid procedure (20) were unsuccessful, therefore the procedure was modified to employ basic conditions (21), and satisfactory products were obtained. The products were examined by infrared and both proton and carbon magnetic resonance spectroscopy, as well as wet chemical methods, and a degree of between 10 and 30% functionalization of the acrylamide found, depending on the reaction time and method of

time and method of analysis. The average structure for this type of polymer, say 20% cationically functionalized, would be as shown in structure 12. Further work on the Mannich products of polyacrylamide

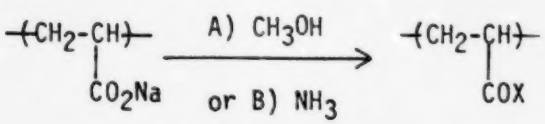


12

will be continued.

b) Conversion of partially hydrolyzed polyacrylamide to neutral polyacrylamide:

The difficulty of obtaining satisfactory molecular weight determinations of polyelectrolytes by viscometric means made a procedure to convert partially hydrolyzed polyacrylamide to a neutral polymer desireable (see equation 8).



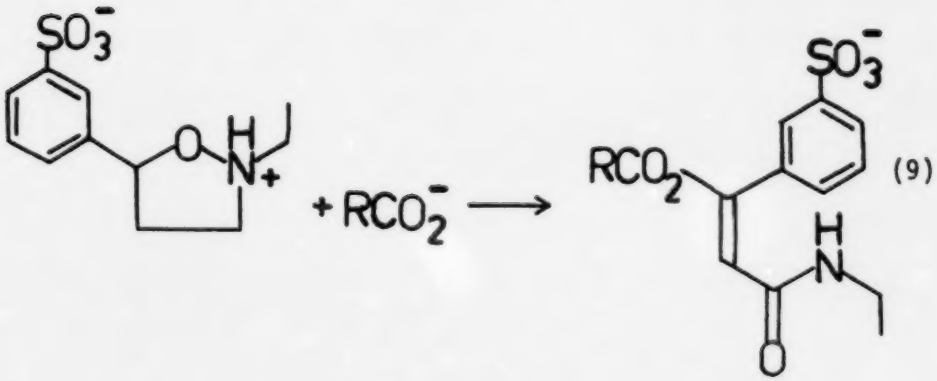
(8)

A; X = OCH_3

B; X = NH_2

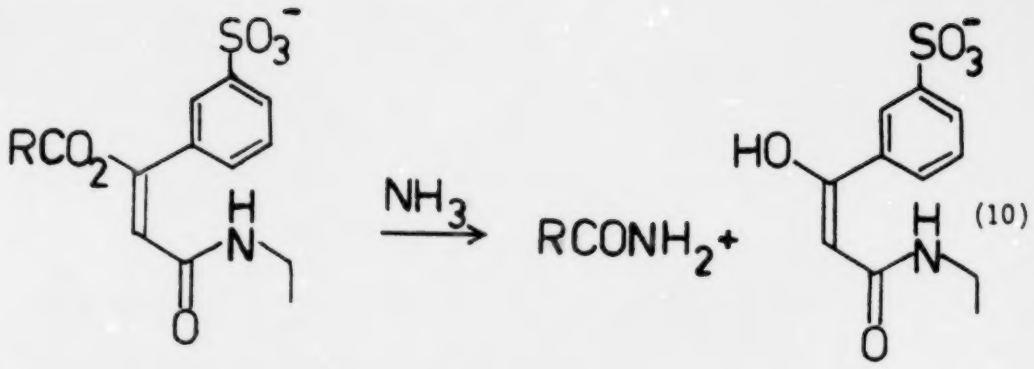
The first procedure attempted, treatment of the polymer with acidified methanol, failed due to the insolubility of the polymer. Other procedures involving initial conversion of the sodium carboxylate form of partially hydrolyzed polyacrylamide to the carboxylic acid form, with subsequent treatment by oxallyl chloride to form the acid chloride, and addition of ammonia to make the amide, failed as well.

One method that showed some success first reacted the carboxylic acid salt with Woodward's Reagent K (22), as shown in equation 9.



(9)

Addition of excess ammonia to the ester product yielded the desired product, as shown in equation 10. No more than half of the carboxylate functionalities of the polymer could be converted to amide, however,



(10)

thereby failing to reach the original requirements of this procedure. Since this time, the purchase of a low angle laser light scattering photometer has rendered visometric determination of molecular weight less important, eliminating the necessity of obtaining neutral polymers for molecular weight determinations.

2) Synthesis of Polymers

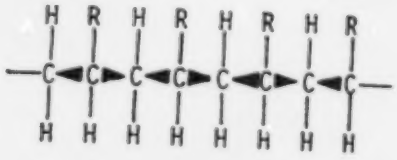
a) Preparation of High Molecular Weight Polyacrylamide Standards:

Polyacrylamide was prepared by the free radical polymerization of acrylamide in a special apparatus designed by Dr. A.E. Hamielec and co-workers (23, 24). Yields of between 36% and 68% of high molecular weight polymer were obtained under different reaction condtions.

Determination of intrinsic viscosity yielded a number average molecular weight of between 1.1 and 1.2 million. These synthetic polymers were found to be pure by spectral and Kjeldahl nitrogen determination analyses, and have been repeatedly employed since their preparation as high purity standards.

b) Preparation of Polymers of Known Stereochemical Structure:

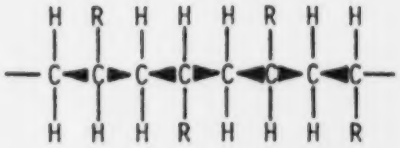
The properties of vinyl polymers such as polyacrylamide depend strongly on the exact stereochemistry of the polymeric chain. Essentially all vinyl polymers form by heat-to-tail linkages, so the backbone consists of alternating methylene groups and methine groups bearing a pendent functionality (see 13 and 14). The relative stereochemistry of adjacent methine groups can, however, vary in three easily recognized patterns. First, if the polymeric chain is extended, and all the pendent functional groups (shown as R) are on the same side of the backbone (see structure 13), the polymer has an isotactic



13

structure. If the R groups aternate from side to side of the polymeric backbone, as in structure 14, the polymer has a syndiotactic

arrangement. Finally, if the R groups are found on both sides of the backbone with no regular pattern, the polymer is termed atactic.



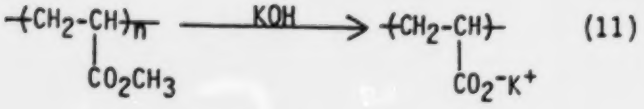
14

Polymers with a stereoregular structure, that is, either an isotactic or syndiotactic arrangement, are usually crystallizable and difficultly soluble materials, whereas irregular or atactic polymers are easily soluble in appropriate solvents, and rarely crystallize (25).

The stereochemical structure of polyacrylamide has not been extensively studied, but is usually assumed to be atactic (26). To confirm or refute this assumption, spectroscopic analysis of the backbone of the polymer offers the most reliable method. However, as the spectroscopic analysis of polyacrylamide is as yet undeveloped, comparison of reaction products of polyacrylamide with similar products prepared from polymers of known stereochemical configuration offered the best method of investigation.

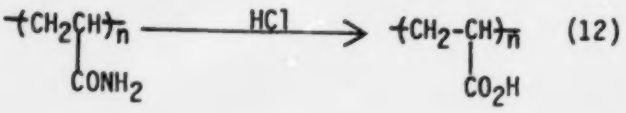
Accordingly, samples of both atactic polymethylacrylate (27) and isotactic polymethyl acrylate (28) were prepared according to published

procedures and their structures confirmed by proton and carbon magnetic resonance spectroscopy. Both of these polymers were then hydrolyzed by ethanolic potassium hydroxide (29) as shown in equation 11. A



(11)

commercial sample of polyacrylamide was hydrolyzed in aqueous acid, as shown in equation 12, and converted to the sodium salt by addition of



(12)

sodium hydroxide. These three sodium polyacrylates were investigated by high resolution proton magnetic resonance spectroscopy, which failed to detect any differences, and carbon magnetic resonance spectroscopy, which clearly differentiated atactic and isotactic sodium polyacrylates.

Other workers (30) have found that the position of the carbon resonance of the methine group varied depending on whether the methine group was isotactic, that is, flanked by methine groups of identical stereochemistry, or heterotactic, flanked by one similar and one dissimilar methine group, or syndiotactic, where the methine group is

flanked by two dissimilar methine groups (see diagram 3). Figures 12, 13 and 14

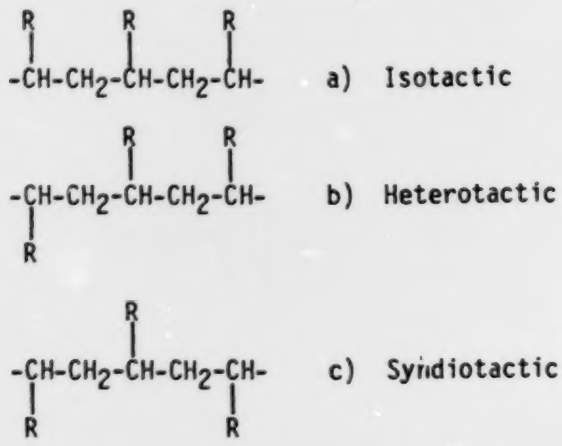


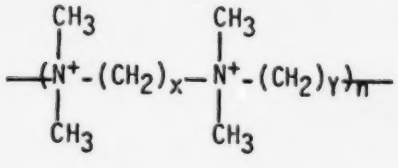
Diagram 3: Possible Methine Stereochemical Arrangements

show the carbon magnetic resonance spectrum in the region of interest of isotactic polyacrylate, atactic polyacrylate, and the polyacrylate of unknown stereochemistry derived from polyacrylamide. The isotactic polymer shows a large isotactic methine resonance at 45.11 ppm, with much weaker heterotactic and syndiotactic resonances slightly downfield. Both the known atactic polyacrylate and the product derived from polyacrylamide, Figures 13 and 14, exhibit a strong heterotactic resonance near 46 ppm, with an isotatic resonance upfield and a syndiotactic resonance downfield. The similarity of these spectra represents definitive evidence that both acrylates are atactic, and therefore that the polyacrylamide precursor must also have an atactic

stereochemistry assuming that racemization did not occur during hydrolysis. Attempts to prepare a similar series of reaction products from polyacryloyl chloride were unsuccessful.

c) Preparation of Polyamines:

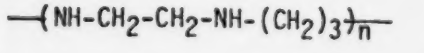
Quaternized polyamines of the general structure 15 represent a common type of cationic flocculant (31). Such polymers are termed



15

X,Y-ionenes, where X and Y denote the number of methylene groups in the two portions of the chain. The simplest ionene would be 2,2-ionene, derived from the methylation of ethyleneimine. Others ranging in structure from 3,3-ionene to 6,6-ionene have also been investigated. In the majority of cases, however, no conclusively identified samples are available, therefore preparation of representative polymers was required.

The polyamine 16 was prepared by the condensation of 1,2-dichlormethane and 1,3-diaminopropane, and satisfactory infrared



16

and nuclear magnetic resonance spectra obtained (see Figures 15 and 16). This material was then treated with dimethyl sulphate to give 2,3-ionene sulphate 17, whose infrared and nuclear magnetic

$$-\left(\overset{+}{N}(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2\text{-}(CH_2)_3\right)_n \quad SO_4^{=}$$

17

spectra are shown in Figures 17 and 18 respectively. The presence of methylene resonances at δ 2.1 and 3.1, and the appearance of a methyl resonance at δ 3.3 represents conclusive evidence of the desired functionalization of the amine groups. The remaining strong resonance at δ 3.7 in the spectrum of the ionene is likely due to unreacted dimethyl sulphate.

The preparation of linear polyamines and ionenes appears well in hand. Analysis of the products' molecular weights will be made once the laser light scattering photometer is operational, and reaction conditions can be adjusted to yield high molecular weight polymer.

CONCLUSION

The development of techniques based largely on infrared and nuclear magnetic resonance spectroscopy and both colloid and conductometric titration has allowed the rapid analysis and classification of flocculant samples as anionic, neutral or cationic. Detailed analysis of the chemical functionalities present in the flocculants has been carried out as well for all anionic, neutral and some cationic flocculants. In outline, the 95 flocculants received can be divided into three groups outlined in Scheme 2. In addition small amounts of unusual termonomer or the presence of inorganic salts have been detected. Finally, the molecular weights of several neutral flocculants was determined by viscometry.

Structure	Ionic Classification			
	Anionic	Cationic	Neutral	Total
Polyacrylamide	52	22	7	81
Polyacrylic acid	2	--	-	2
Polydiallydimethyl-ammonium salt	--	4	-	4
Polyamine	--	8	-	8
Total	54	34	7	95

Scheme 2: Chemical classification of flocculants.

Assessment of factors that could affect flocculant performance found that mild agitation, the presence of dissolved air, and the presence of ferric ion, a mild oxidant, had little degradative effects on neutral or anionic polymers in time spans up to two weeks. The presence of transition metal ions such as iron and copper, and to a lesser degree magnesium and sodium, caused a great decrease in anionic flocculant solution viscosity, presumably due to a tightening and shrinkage of the polyelectrolyte molecules. This conformational change, while not degrading the molecule, may cause changes in flocculating ability.

Synthesis of new polymers by post-modification has yielded cationic polymers from neutral polyacrylamide via the Mannich reaction. Complete synthesis of pure polyacrylamide yielded samples that have been repeatedly used as standards in later analyses. Preparation of polymethyl acrylate of known tacticity and comparison of polyacrylate salts prepared from these polymers and polyacrylamide has given new evidence to the assumption that polyacrylamide is an atactic polymer. Finally, preparation of cationic polyamines and polyquaternary amine salts or ionenes has been commenced. The synthesis of small quantities of both polyamine, ionene, and cationic polyacrylamides is important as no commercial standards are presently available.

EXPERIMENTAL

CONDUCTOMETRIC TITRATION WITH SODIUM HYDROXIDE OF THE ELUENT FROM A CATION EXCHANGE COLUMN AFTER ADDITION OF SAMPLE 3

SCOPE: Estimation of degree of hydrolysis of anionic flocculants.

PROCEDURE:

First Method: A total of 0.100 gm of sample 3 was added slowly to 100 mls of rapidly stirred distilled water, and the stirring of the covered beaker continued for between 4 and 18 hours.

Meanwhile, approximately 16 gms of the ion exchange resin Dowex 50W-X8 (capacity, 5.1 milliequivalents per gm of resin) was washed successively with 100 ml quantities of distilled water, 4M hydrochloric acid, distilled water, 2M hydrochloric acid, distilled water, 0.5M sodium hydroxide, distilled water, and 2M hydrochloric acid. The resin was poured into the column (1.5 x 30 cm, with a solvent reservoir on top), and 100 mls of 2M hydrochloric acid was added and allowed to run through. The column was now washed with distilled water until the pH rose to 5.

The solution of sample 3 was now added to the top of the column, and allowed to flow through at up to 2 drops per second. Normally the higher viscosity of the flocculant solution lowered the flow rate well below this figure; occasionally a positive pressure of nitrogen was

applied to the column to increase the flow. Distilled water was added after elution of the flocculant solution until the pH reached 5. The column was usually reused once, by recharging with 100 mls 2M hydrochloric acid, and washing with distilled water until the effluent reached pH 5.

The eluted flocculant and washings were titrated with 0.100 M sodium hydroxide (Fisher Chemical Company), using a Radiometer conductivity meter Model CDM 2 d to determine the solution conductivity.

Second Method: This procedure was repeated with 15 mg sodium sulphate added to the original flocculant solution of sample 3 immediately after addition of the flocculant to water.

CALCULATION OF THE EXTENT OF HYDROLYSIS, AND THE AMOUNT OF SODIUM SULPHATE PRESENT

The data obtained by the second method described was plotted (see Figure 10 for a similar example) and the end-points, say 2.50 mls and 5.65 mls, were determined by extention of the straight-line portions of the graph to an intersection point. The amount of added base at the first end-point, 0.25 mmoles (2.5 mls x 0.100M sodium hydroxide), corresponded to the total amount of strong acid present in the eluent. The 15 mg of sodium sulphate added would have accounted for 0.211

mmoles of the acid eluted, leaving 0.039 mmoles of strong acid. If this were due to sodium sulphate in the original sample of flocculant, then 0.0195 mmoles of sodium sulphate or 2.77 mg must have been present in the original sample of 100 mg, a total of 2.8% by weight.

The difference between the first and second end-point, 3.15 mls, would correspond to 0.315 mmoles of weak acid. The total weight of polymer, after correction for the amount of water (4.5% of 100 mg) and sodium sulphate (2.8% of 100 mg) present, was 92.7 mg. Thus it remains to determine the average molecular weight of the mixture of monomers that make up the polymer, and the total number of mmoles of the monomer present could be calculated. As the molar amount of hydrolyzed polyacrylamide is known, the extent of hydrolysis could be found.

It is known that all of the carboxylic acid in this flocculant was present as a sodium salt. So the flocculant would have an average monomer molecular weight between 71, the moluecular weight of acrylamide, and 94, the molecular weight of sodium acylate. The simplest procedure for determination of the average monomer molecular weight, although tedious, is a simple reiterative procedure.

Thus the average monomer molecular weight was assumed to be 71 for sample 3. As 92.7 mg were known to be present, the total number of mmoles of flocculant would be 1.31 mmoles. As 0.315 mmoles of weak acid were known to be present, the extent of hydrolysis can be found to be:

$$\frac{0.315}{1.31} \times 100 = 24.1\%$$

This value could now be used to find a corrected average monomer molecular weight. Thus, as 24.1% of the monomer had a molecular weight of 94 and 75.9% was of molecular weight 71, then

Average MW = (0.241 x 94) + (0.759 x 71) = 76.5

This was then used to find adjusted values for the total amount of monomer present (1.21 mmoles), and therefore new values for the extent of hydrolysis (26.0%). Repetition of the cycle four times gave values of 26.2% hydrolysis, based on an average molecular weight of 77.0. Any desired degree of accuracy can be obtained by repeated iterations of the calculations, but calculations yielding more than three significant figures would exceed the limits of accuracy of the data.

USE OF COLLOID TITRATION

SCOPE Estimation of ionic functionality on polymers by a method used to determine colloidal charge.

REAGENTS Indicator: Toluidine Blue 0.050 g/500 ml dist. H_2O; deep purple colour.

Internal stand.: PolyDADMAC mwt. 161, available as a 15% wt/vol H_2O solution 1.0733 g 15% solution diluted to 1 l. (0.001N).

Titrant: PVSK mwt. 162, available as dry powder; .1620 g dissolved in 1 l. deionized water to give 0.001N solution.

PROCEDURE Fifty mg of the undried sample was dissolved in approx. 50 ml deionized water by stirring and the solution was transfered into a 100 ml volumetric flask and diluted to 100.0 ml. Exactly 1 g of this solution was weighed into a plastic 250 ml beaker and the sample was titrated.

A 1 g sample of 0.05% solution is weighed into a beaker and diluted with 100 ml deionized water, 10.0 ml of 0.001N DADMAC is added, and the volume recorded as A. This solution is adjusted to pH 4.0 for cationic polymer using dilute HCl. Two drops of indicator are added to give a blue solution (in case the solution remains purple a known amount of DADMAC is added and has to be accounted for in volume A). While stirring with a magnetic stirrer, the solution is titrated with 0.001N PVSK to a blue violet end-point that persists at least 15 seconds. The volume is recorded as B. This procedure was repeated. A blank titration of 100 ml H_2O plus A ml DADMAC, adjusted to the appropriate pH, is made to the same colour end-point as the sample. Record volume of titrant as C.

CALCULATION $\frac{\text{(mg sample)}}{\text{(B-C) (0.001M)}} = \text{equivalent weight}$

$\frac{1000}{\text{equivalent weight}} = \text{milliequivalents per gram}$

EXAMPLE: The analysis of sample 10 according to the above procedure yielded the following:

B-C = 1.60 mls

Sample 10 contains 3.7% water, thus the total flocculant present in the 1 ml aliquot tested is:

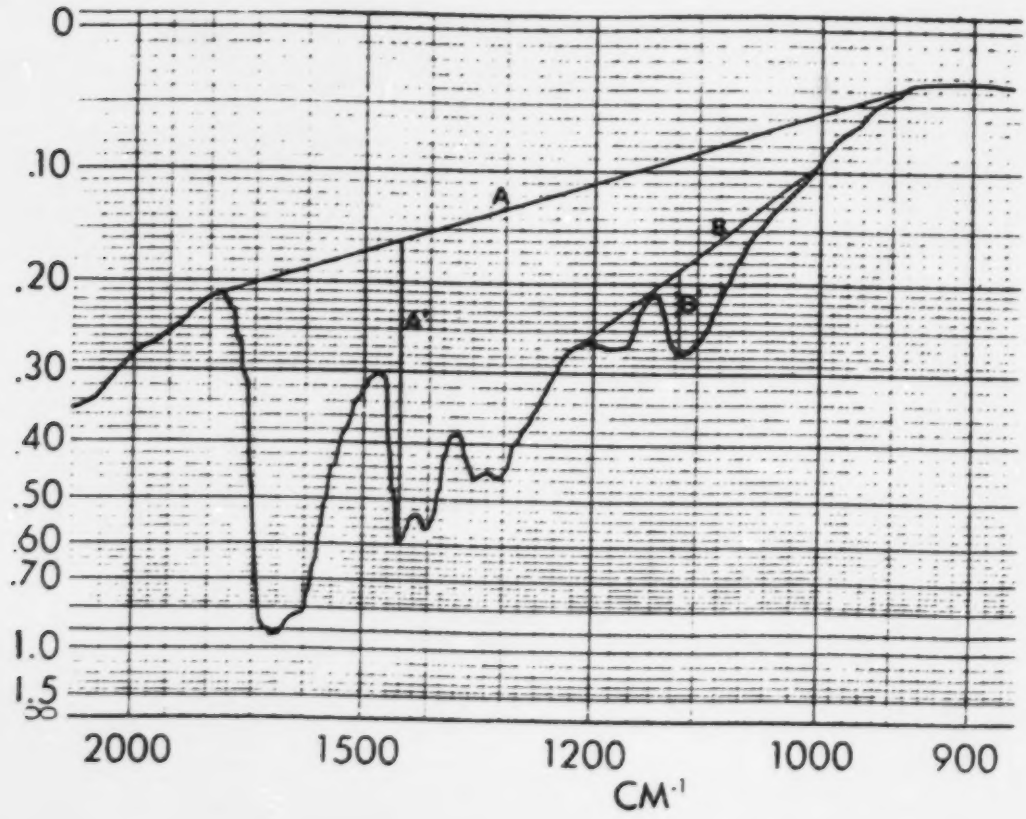
$\frac{50 \times .963}{100} = 0.4815 \text{ mg}$

$\text{equivalent weight} = \frac{0.4815 \text{ mg}}{(1.6 \text{ mls}) (0.001 \text{ mequiv/ml})} = 301 \text{ mg/mequiv.}$

$\text{milliequivalent per gram} = \frac{1000 \text{ mg/gm}}{301 \text{ mg/mequiv}} = 3.32 \text{ mequiv/gm}$

DETERMINATION OF SULPHATE CONTENT BY QUANTITATIVE INFRARED SPECTROSCOPY

An infrared spectrum of the sample in question is taken using the absorbance mode of the spectrophotometer. The region between 200 cm^{-1} and 900 cm^{-1} is usually satisfactory for this analysis.



The points of minimum absorption near 200 and 900 cm^{-1} are connected by a straight line 'A', which acts as a base line. A second line 'A^1' is dropped vertically from Line 'A' to the absorption

maximum at or near 1440 cm^{-1}. The absorbances at the points that 'A^1' intersects the spectrum trace (0.60) and the base line 'A' (0.16) are noted, and the difference (0.44) found. This is the corrected reference absorbance.

Similarly, the minima near 1200 cm^{-1} and 1000 cm^{-1} are connected by a line 'B', and a vertical 'B^1', is dropped to the maximum absorption near 1120 cm^{-1}. The absorbances at the intersects of 'B^1', and the spectrum trace (0.29) and 'B^1' and the base line 'B' (0.19) are noted, and the difference (0.09) found. This is the corrected sulphate absorbance.

Finally, the ratio between the corrected sulphate absorbance and the corrected reference absorbance is found - 0.09 + 0.44 = 0.205. This absorbance ratio is used to calculate the uncorrected sulphate content:

$$\% \text{ sulphate} = 18.0 \times \text{absorbance ratio} - 3.0$$

Thus the absorbance ratio 0.205 yields 0.7% sulphate. This relationship yielded results within 4% sulphate content in 9 out of 10 samples tested.

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TABLE 1

Characteristic infrared absorptions of various flocculant functionalities.

Functionality	Infrared Absorptions (cm^{-1})
Amide	3400 - 3200, 1650, 1600
Carboxylate	1550, 1400
Carboxylic acid	3000 - 2100, 1700
Amine	3300, 1650, 1150
Quaternary amine	1440, 950
Inorganic sulphate	1100

TABLE 2

Characteristic nuclear magnetic resonances of various flocculant functionalities.

Functionality	Resonance (δ)
Polyacrylamide backbone	1.7, 2.1
Methyl ester	3.7
Alkyl quaternary ammonium salt	3.0 - 3.5
Protonated alkyl amine	3.0 - 3.5
Alkylamine	2.2 - 2.5

TABLE 3

Comparison of the degree of hydrolysis of anionic flocculants as determined by Fourier transform carbon-13 magnetic resonance and conductometric titration.

Sample	% Hydrolysis by CMR	% Hydrolysis by conductometry
2	46.8	47.2
4	0	0
15	23.0	18.9
39	0	5.4
49	60.0	63.0

TABLE 4

Chemical characteristics of cationic polyacrylamide-based flocculants.

Sample	%Volatiles	Cationic functionalities (mequiv/g)		%N
		Colloid	Conductometric	Kjeldahl
5	55.6	1.3	3.2	10.8
10	3.4	2.3	2.2	13.0
19	35.5	0.1	-	7.8
22	90.9	4.1	2.7	11.3
23	9.2	0.2	0.9	18.3
25	9.7	1.1	1.2	17.1
53	81.8	5.1	6.0	19.1
62	8.3	0.6	-	15.7
63	9.2	2.4	-	12.5
64	9.3	1.4	-	9.6
69	3.8	0.8	1.5	15.2
70	3.9	1.3	2.1	14.1
71	5.4	1.1	1.9	14.5
74	6.3	0.4	1.8	17.4
75	4.6	1.8	2.5	13.5
77	6.9	1.5	1.2	11.2
85	5.1	0.7	1.4	15.8
87	60.7	2.2	1.9	9.53
88	10.2	3.5	1.4	9.1
90	95.9	3.3	-	14.9
92	6.1	1.2	2.4	13.8
95	89.9	2.5	0	9.9

TABLE 5

Chemical characteristics of polyamine-based cationic flocculants.

Sample	%Volatiles	Cationic functionalities (mequiv/g)		%N
		Colloid	Conductometric	Kjeldahl
6	10.2	4.2	1.0	5.2
9	58.8	11.2	3.8	10.2
14*	78.4	5.2	0	8.0
16	49.5	6.8	3.4	9.7
20	50.4	6.2	3.4	9.8
24	56.8	2.0	0.6	4.7
56*	78.3	5.5	0	8.0
57*	78.6	4.6	0	7.7
86	75.0	4.8	2.3	5.8
89*	82.9	6.4	3.3	8.0
91	75.2	6.7	6.8	11.2
94	74.3	6.6	4.3	9.2

* Polydiallyldimethylammonium-based polymer.

TABLE 6

Chemical Characteristics of polyacrylamide-based anionic flocculants.

Sample	pH	% Hydrolysis conductometry	%N Kjeldahl	% Salt
1	6.1	7.1	17.4	0.7
2	8.8	39.6	8.4	2.8
3	9.9	26.3	10.3	3.1
7	6.8	13.6	15.4	1.2
8	7.0	29.5	11.0	1.1
11(A)	6.5	92+	0.6	---
12	6.6	5.5	18.2	1.8
13	9.4	20.8	13.4	3.2
15	7.2	18.0	13.9	7.5
17	7.1	5.0	18.9	1.1
18	7.4	32.0	11.8	2.8
21(K)	7.5	35.6	9.6	3.6
26	6.5	15.2	16.0	1.5
27(N)	6.0	51.6	13.6	0.8
28	5.6	5.1	15.5	19.6
29(K)	7.1	19.0	15.3	1.8
31	7.1	38.0	12.2	1.5
33	6.1	19.1	14.0	0.7
34	8.9	35.4	9.1	12.7
35	7.7	9.6	16.0	3.2
36	9.8	26.7	12.6	3.9
37	6.3	5.8	18.3	0
38	6.9	11.0	17.3	4.3
39	6.9	5.4	17.6	3.7
40	6.8	4.5	18.2	3.2
41	9.3	24.2	10.9	8.3
42	7.1	24.6	12.9	2.8

Table 6 continued

Sample	pH	% Hydrolysis conductometry	%N Kjeldahl	% Salt
44	4.5	4.4	18.3	3.5
45	9.6	14.6	14.7	3.5
46	6.3	6.5	17.4	3.5
47	6.4	8.0	17.4	3.5
48	9.5	28.8	10.7	4.6
49	8.1	63.0	4.0	5.3
50	9.4	18.9	11.7	7.1
51	7.1	8.4	18.5	2.8
52	8.9	20.1	14.2	2.8
55	9.3	20.0	11.7	10.6
58	6.8	10.5	13.8	2.1
60	6.7	15.1	13.8	0
61	6.5	6.7	17.2	0
65	5.8	7.7	15.4	5.0
66	6.6	7.8	16.3	2.5
67(K)	7.6	34.5	10.2	11.9
68	6.3	10.0	15.5	0
72	8.1	18.6	13.6	0
73(A)	6.6	73.9	0.6	-
76	5.9	4.0	15.0	17.3
78(K)	7.3	35.9	8.4	1.7
79	7.0	31.5	11.0	5.8
80	7.0	22.3	12.1	6.0
81	9.7	29.2	10.0	3.2
82	7.6	9.7	15.5	2.8
84	9.5	22.3	12.0	2.5
93	7.2	17.5	15.3	2.8

A - flocculant is sodium polyacrylate

K - flocculant contains substantial amounts of potassium cation

N - flocculant contains only ammonium cation

TABLE 7

Chemical characteristics of polyacrylamide-based neutral flocculants.

Sample	pH	% N Kjeldahl	% Salt
4	5.9	18.0	7.6
30	5.7	10.3	45.8
32	6.1	14.0	0.7
43	5.9	18.8	0.7
54	7.0	18.6	1.4
59	6.1	18.0	0
83	6.9	16.8	2.8

TABLE 8

Content of ammonium cation in anionic flocculants.

Sample	% NH_4
12	0.24
17	0.47
26	0.63
27	2.59
29	0.46
31	1.28
38	0.51
39	0.24
41	0.25
44	0.39
46	0.28
51	0.22
61	0.24
65	0.31
66	0.28

TABLE 9

Molecular weight of certain neutral flocculants determined by different methods.

Sample	Viscosity Mn x 10^6	GPC Mn x 10^6	GPC Mw x 10^6
4	5.1	3.95	6.4
30	-	7.6	14.6
43	5.0	3.3	7.0
54	12.9	4.5	9.3
59	9.0	--	--
83	20.0	--	--

TABLE 10

Chemical characteristics of named polymer samples.

Sample	pH	% Hydrolysis	%N
Polyscience 2220	9.7	25.0	10.8
Polyscience 4652	6.9	19.1	14.7
Dow 87D	6.9	21.3	17.1
Dow XD7321	9.0	81+	0
Hamielec - 24.7%	-	24.7	12.8
PolyHall 402	6.0		-
Alchem 5W3682			
Initiator	-	-	-
Solution	-	-	-
Suspension	8.4	76+	0.4
PDADMAC (cationic)	6.5	6.2 mequiv/g cationic function	8.6

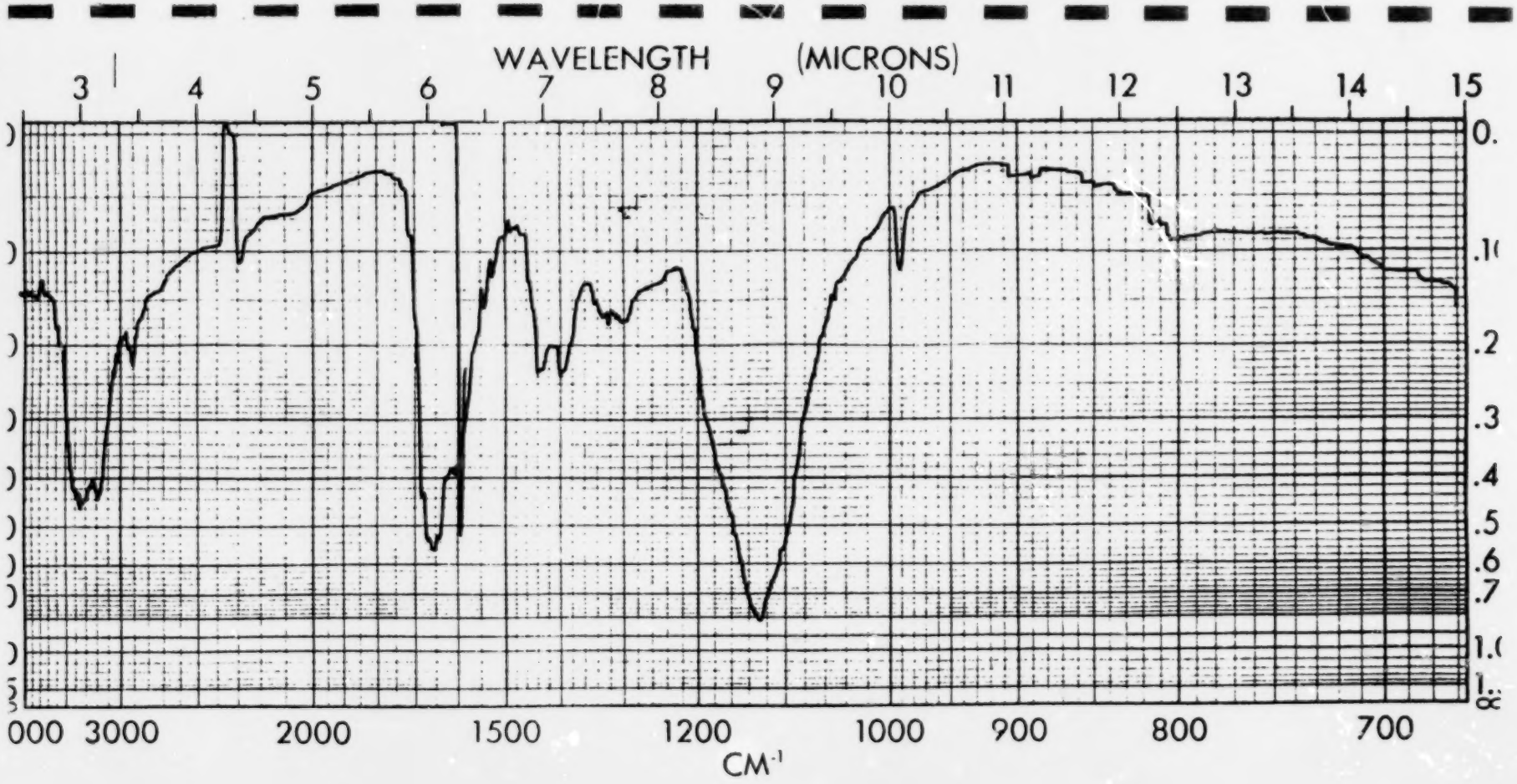


Figure 1: Infrared spectrum of sample 30 (aqueous cast).

3400 - 3200 cm^{-1}; N-H

1660 cm^{-1}; amide

1440 cm^{-1}; C-H

1120 cm^{-1}; sulphate

Reference at 1601 cm^{-1}.

2920 cm^{-1}; C-H

1600 cm^{-1}; amide

1400 cm^{-1}; C-H

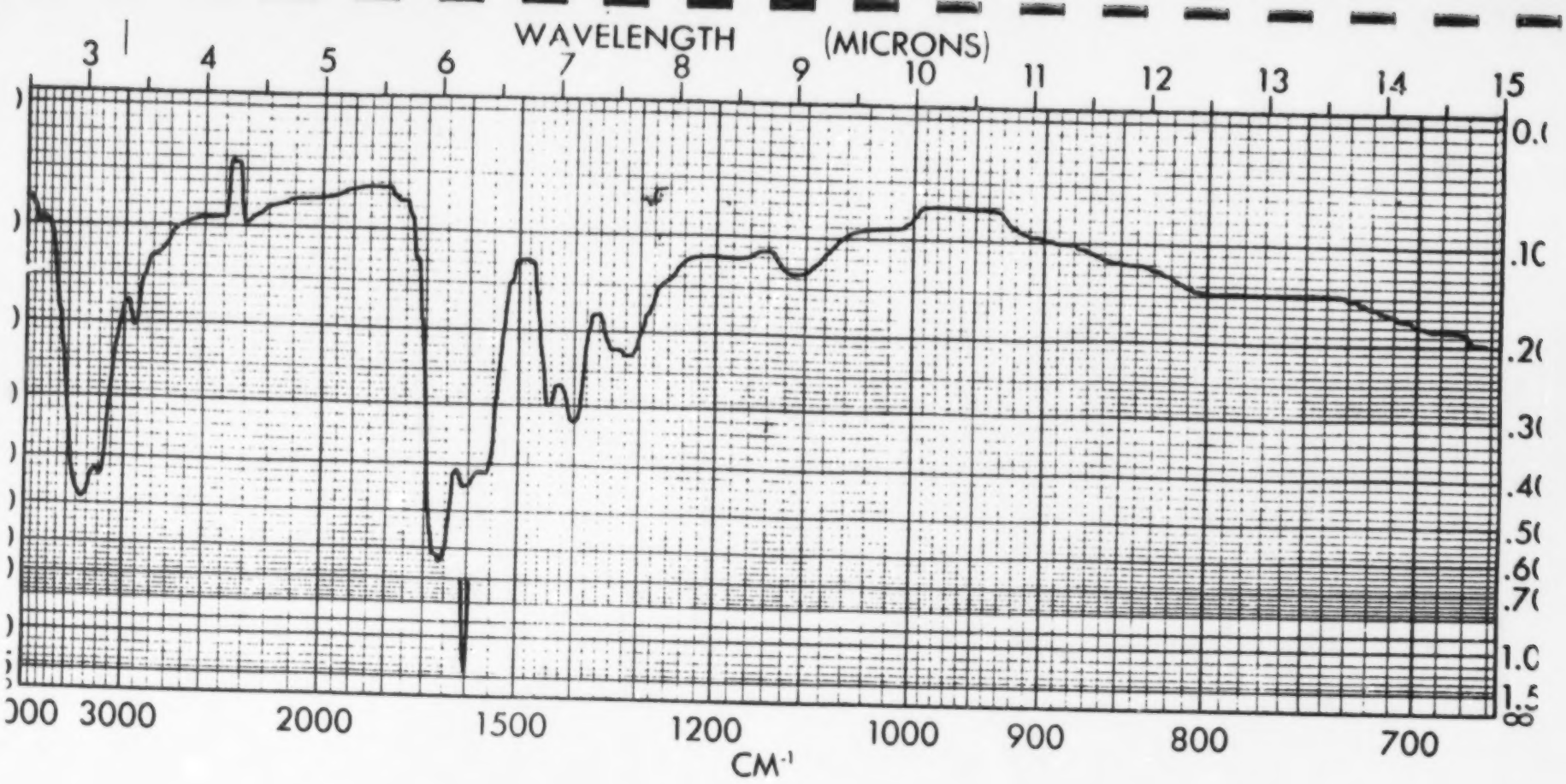


Figure 2: Infrared spectrum of sample 15 (aqueous cast)

3350 - 3200 cm^{-1} ; N - H

1660 cm^{-1} ; amide

1560 cm^{-1} ; carboxylate

1400 cm^{-1} ; C - H, carboxylate

Reference at 1601 cm^{-1}

2910 cm^{-1} ; C - H

1610 cm^{-1} ; amide

1450 cm^{-1} ; C - H

1110 cm^{-1} ; sulphate (?)

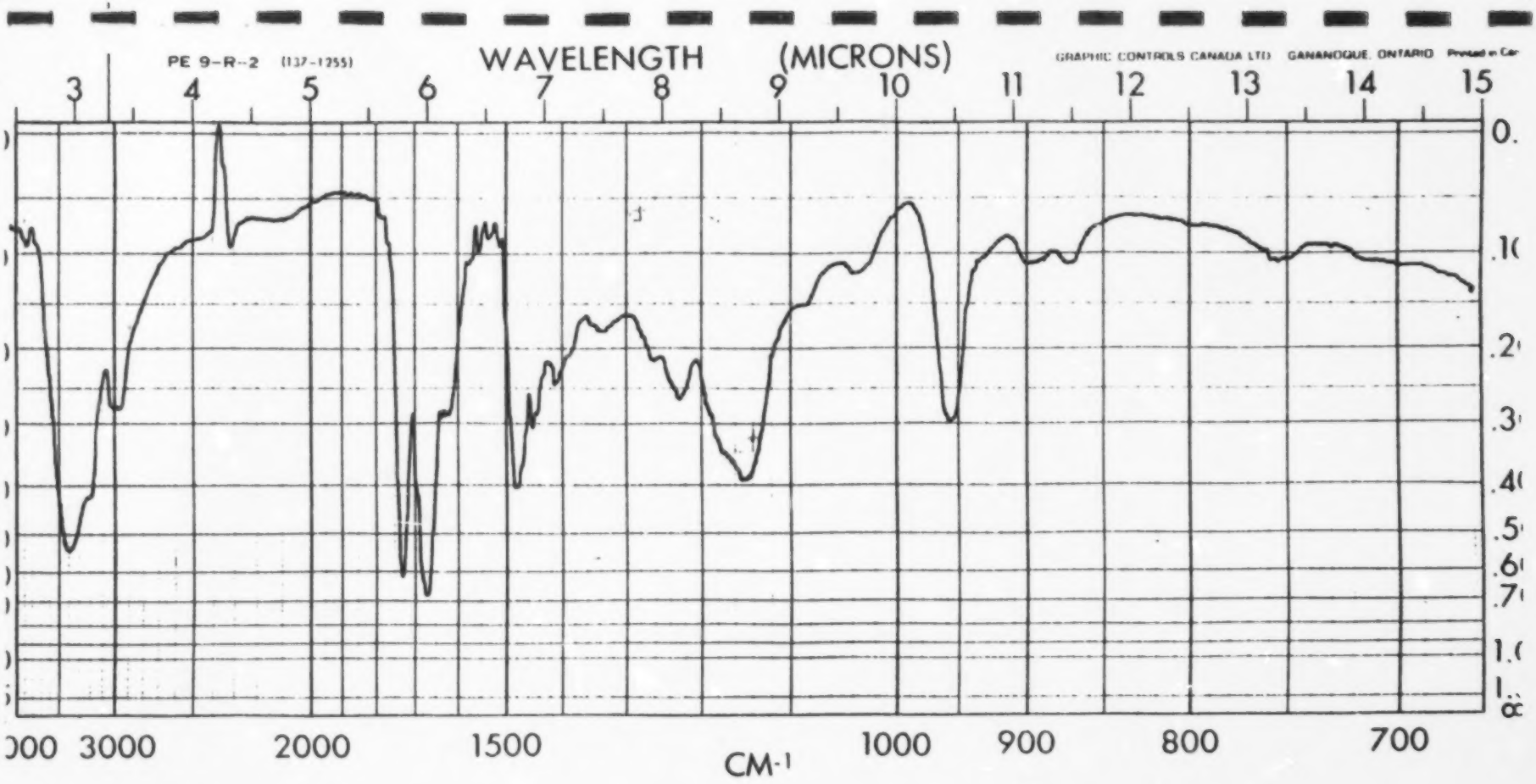


Figure 3: Flocculant sample 88 (aqueous cast)

3400 - 3200 cm^{-1}; N-H

1660, 1620 cm^{-1}; amide

1440, 1400 cm^{-1}; C-H

1730 cm^{-1}; ester

1480, 950 cm^{-1}; $\overset{+}{N}-CH_3$

1140 cm^{-1}; C-N, C-O

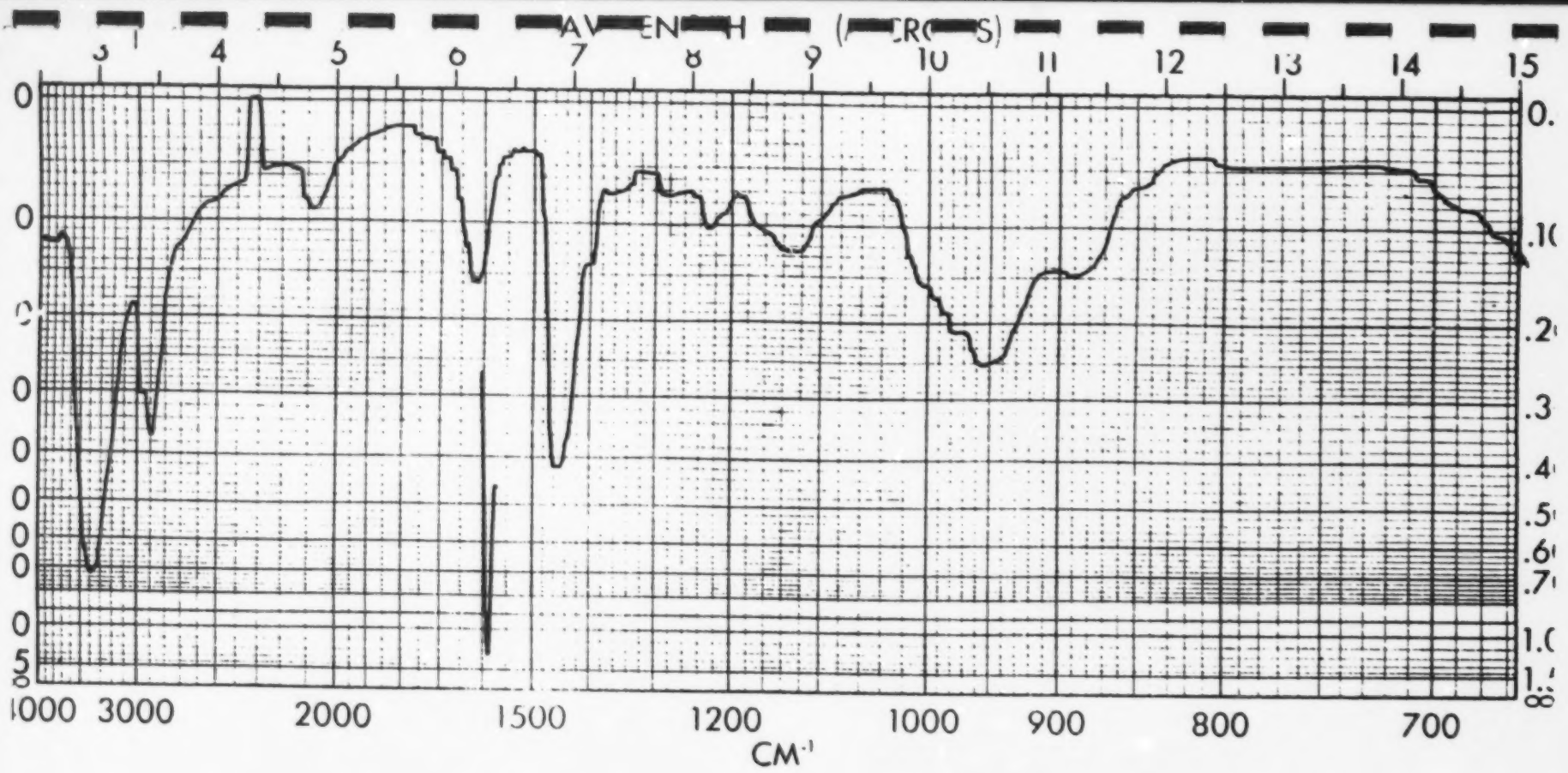


Figure 4: Infrared spectrum of sample 14 (aqueous cast)

$3400\ cm^{-1}$; N - H

$2940\ cm^{-1}$; aliphatic C - H

$1630\ cm^{-1}$; N - H

Reference at $1601\ cm^{-1}$

$3000\ cm^{-1}$; vinyl C - H (?)

+

$2100\ cm^{-1}$; N - H

$1460\ cm^{-1}$; aliphatic C- H

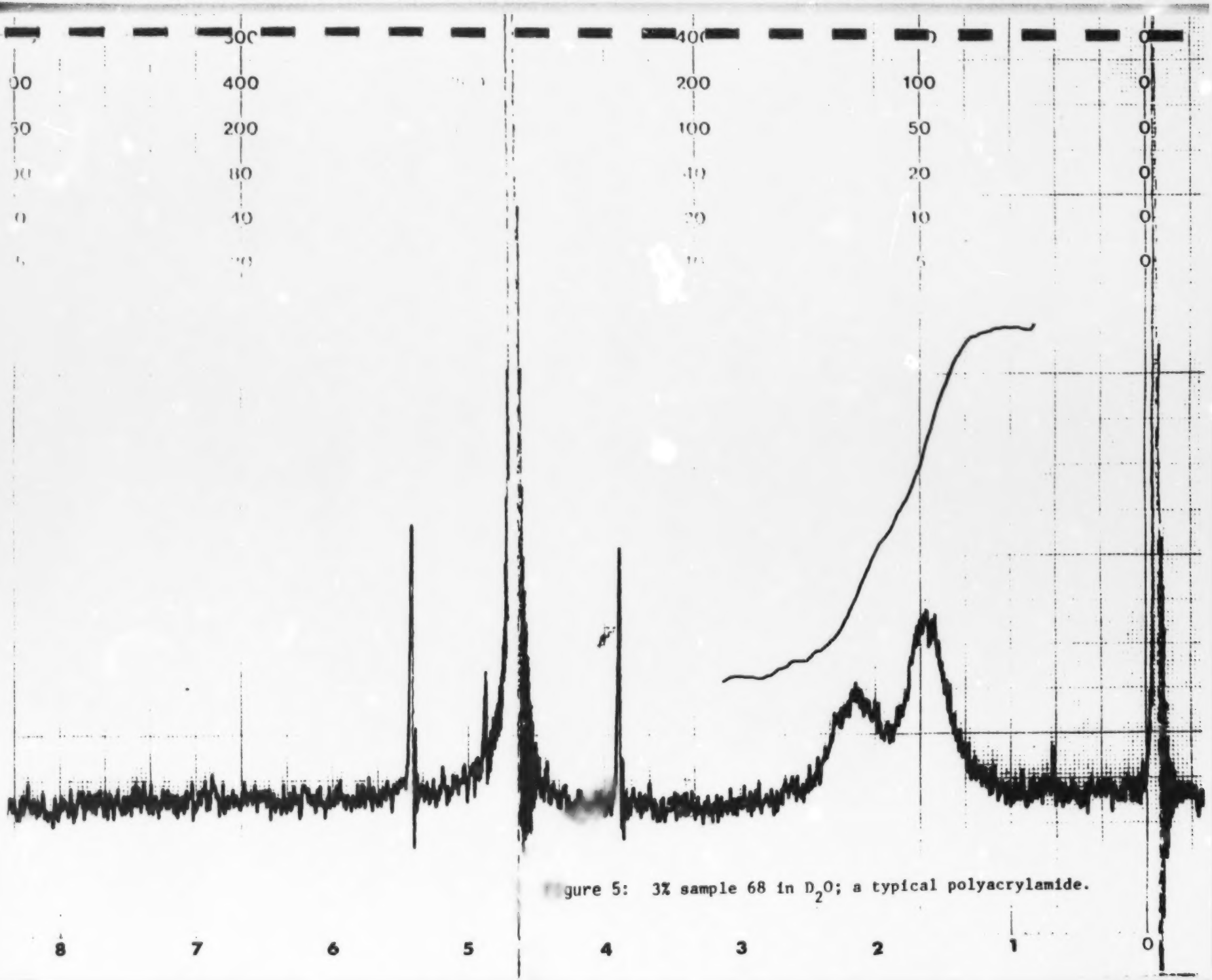


Figure 5: 3% sample 68 in D_2O; a typical polyacrylamide.

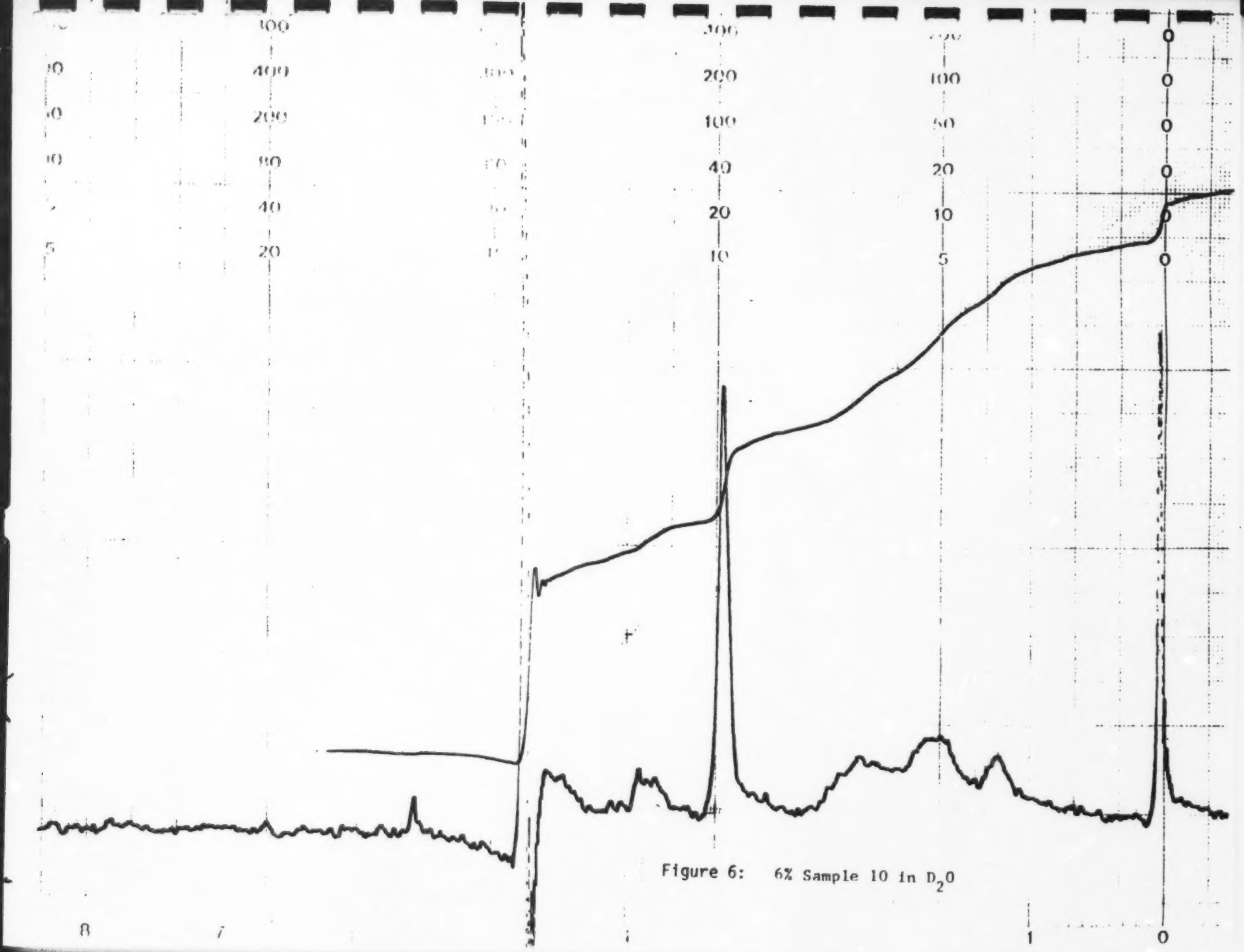


Figure 6: 6% Sample 10 in D_2O

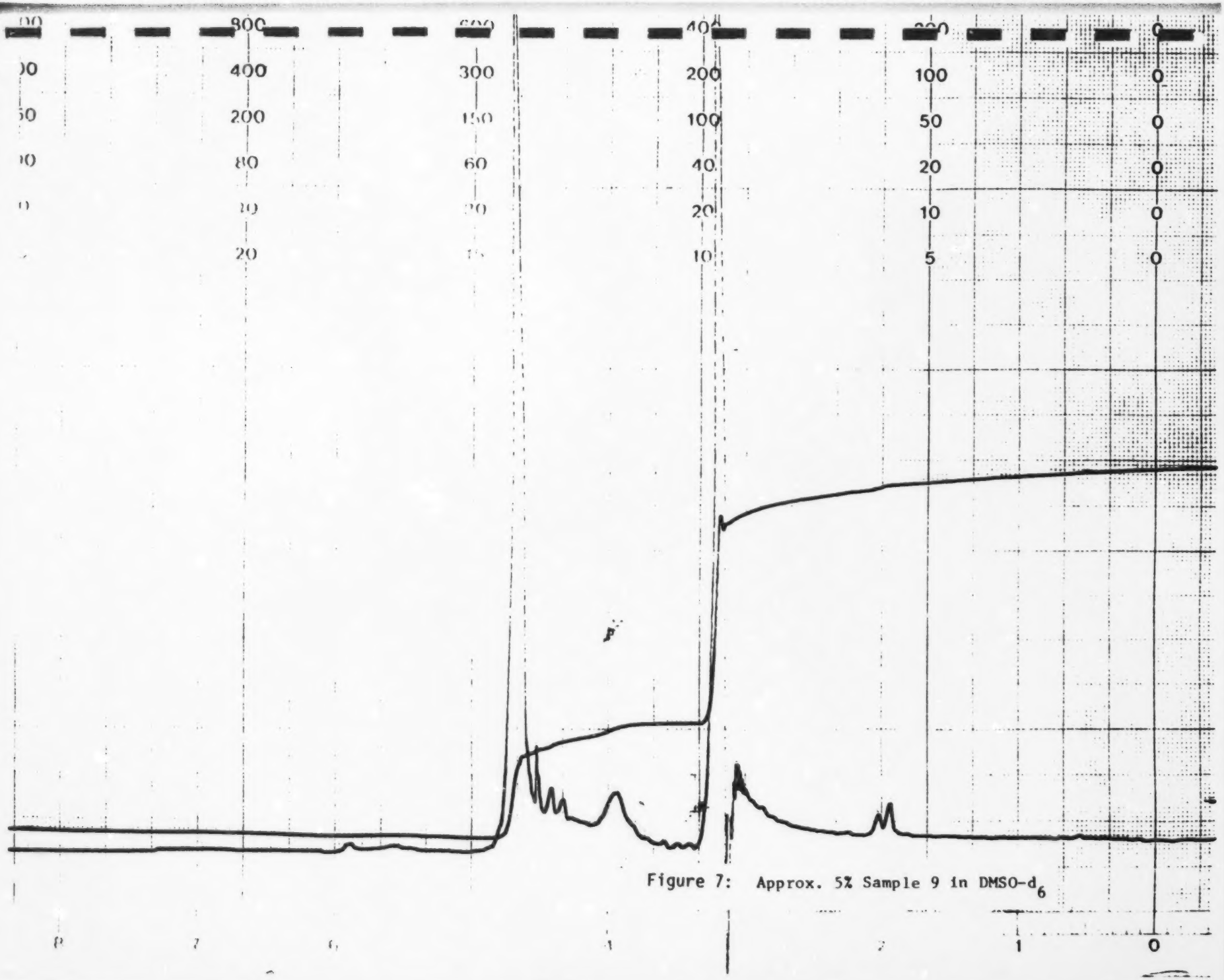


Figure 7: Approx. 5% Sample 9 in DMSO-d_6

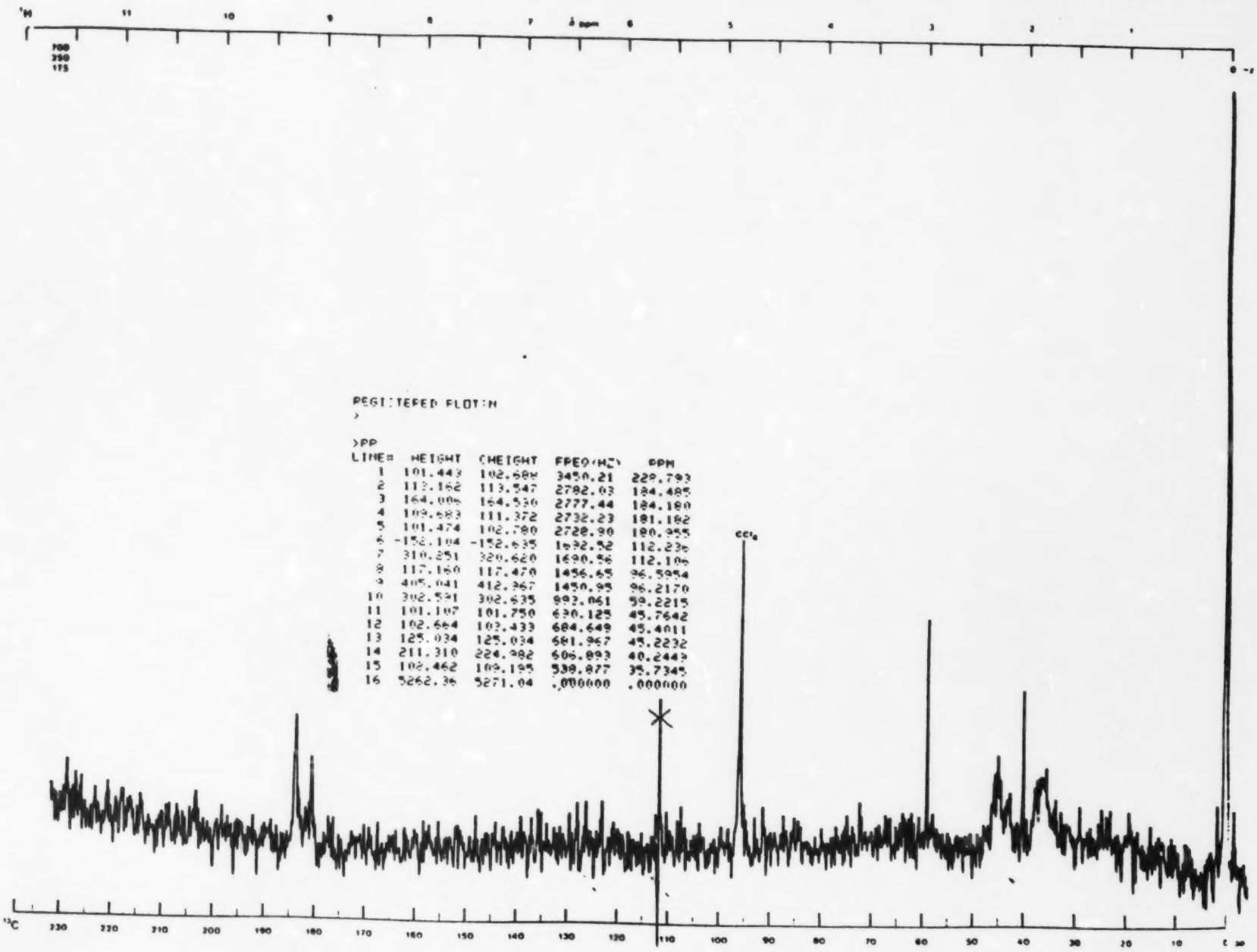


Figure 8: Carbon-13 nmr of sample 49.

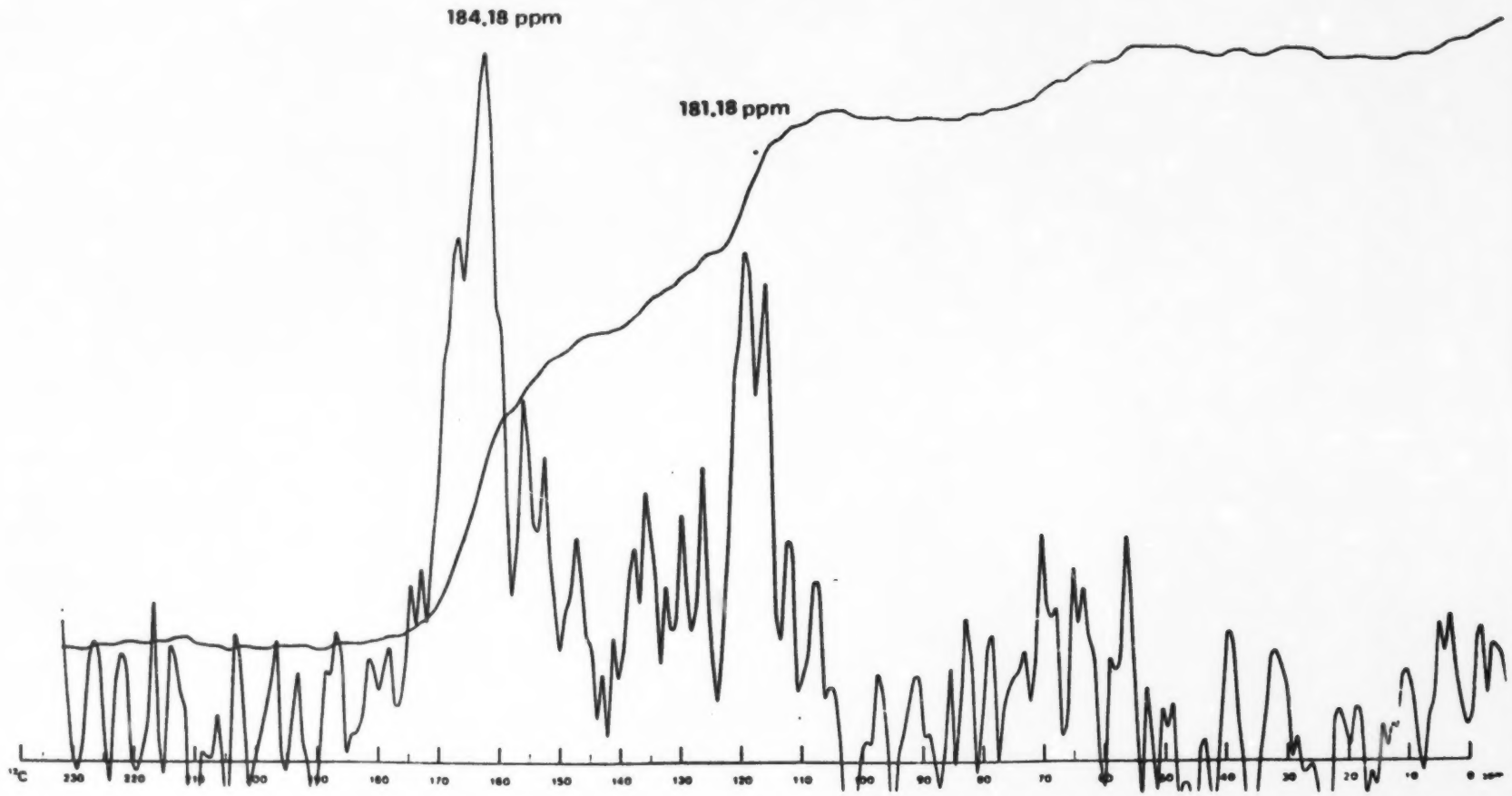


Figure 9: Integration of the carbonyl resonance of sample 49.

Figure 10: Titration of 100 mg sample 31 plus 5 ml 0.1 M HCl with 0.1 M NaOH

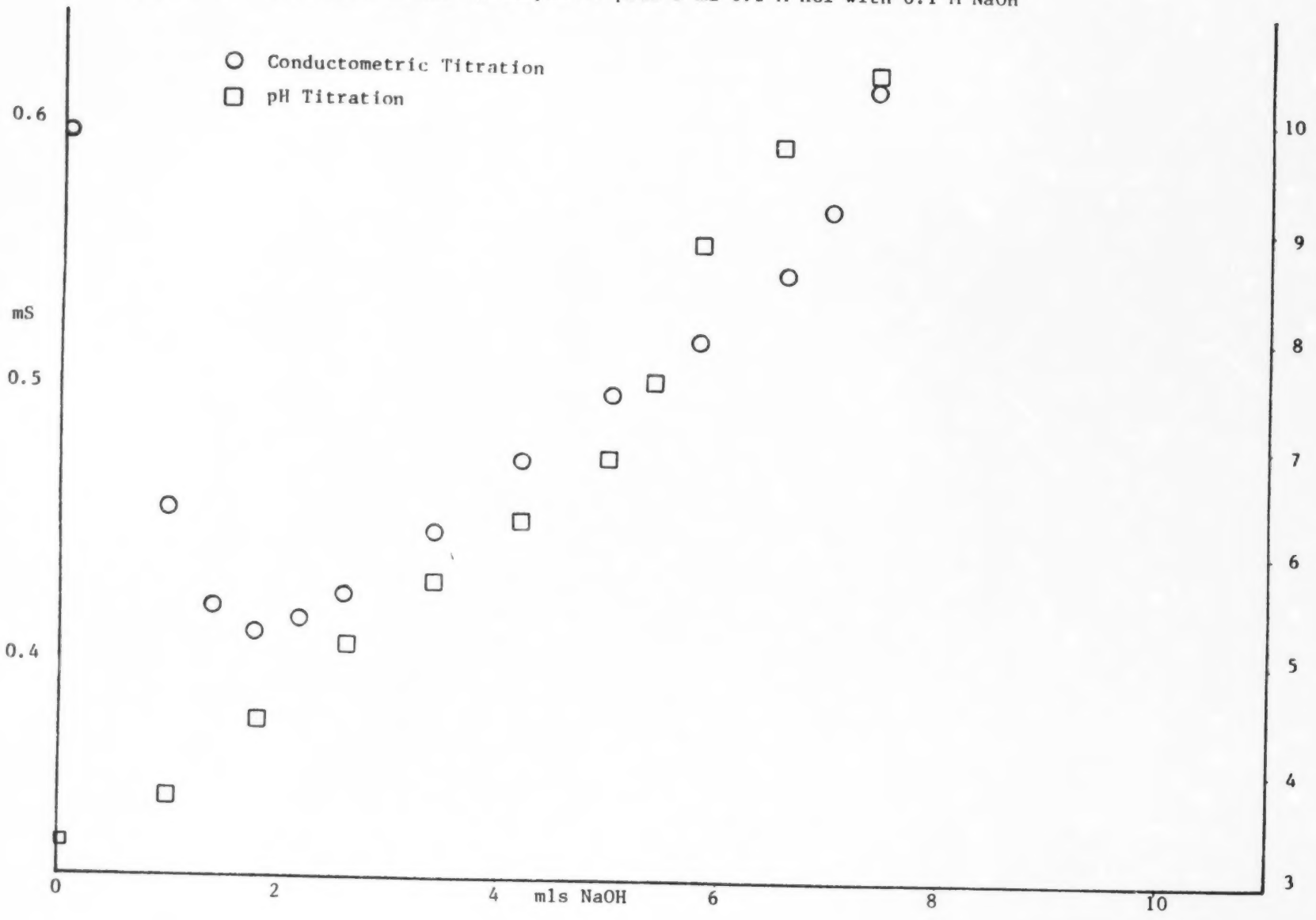
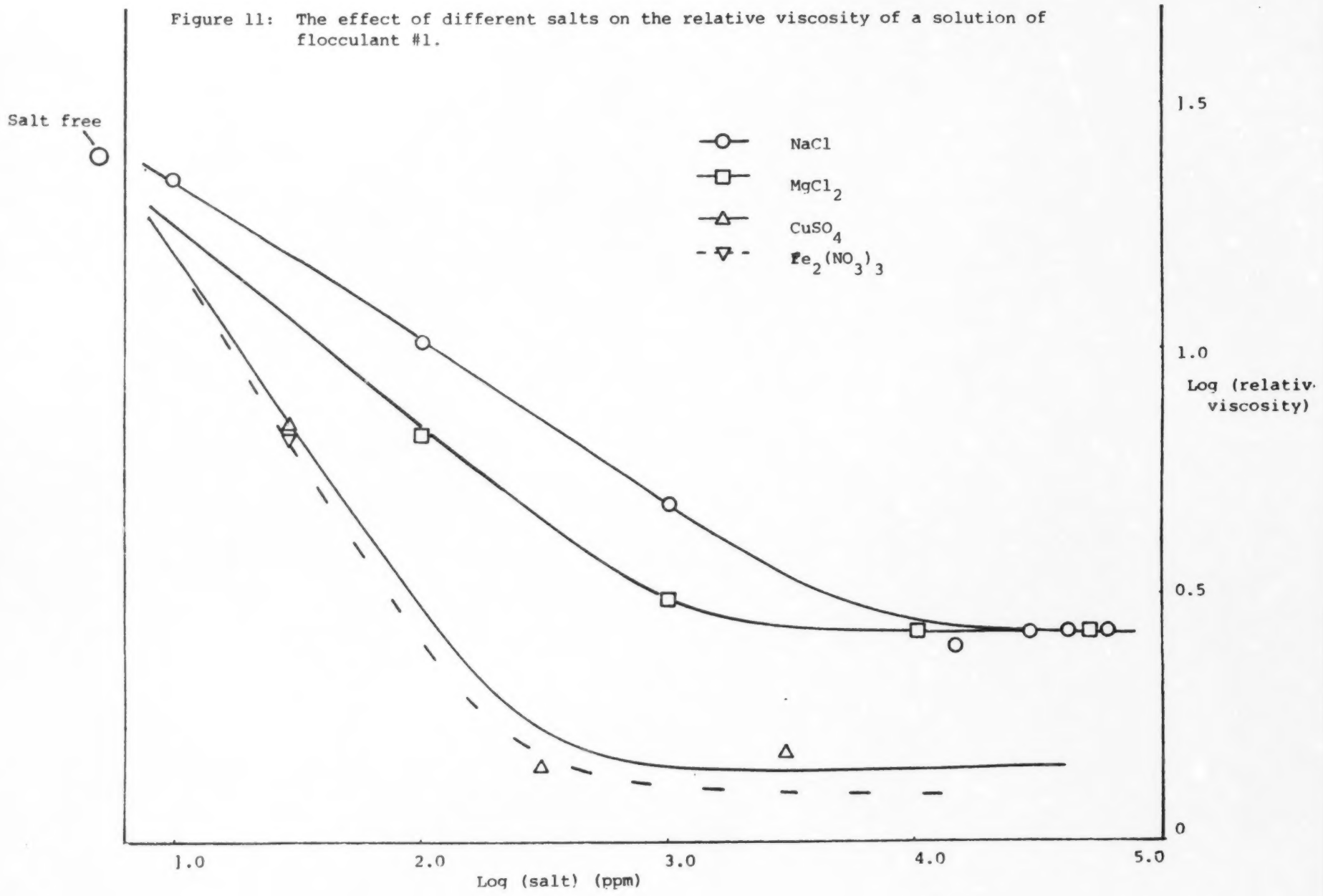


Figure 11: The effect of different salts on the relative viscosity of a solution of flocculant #1.



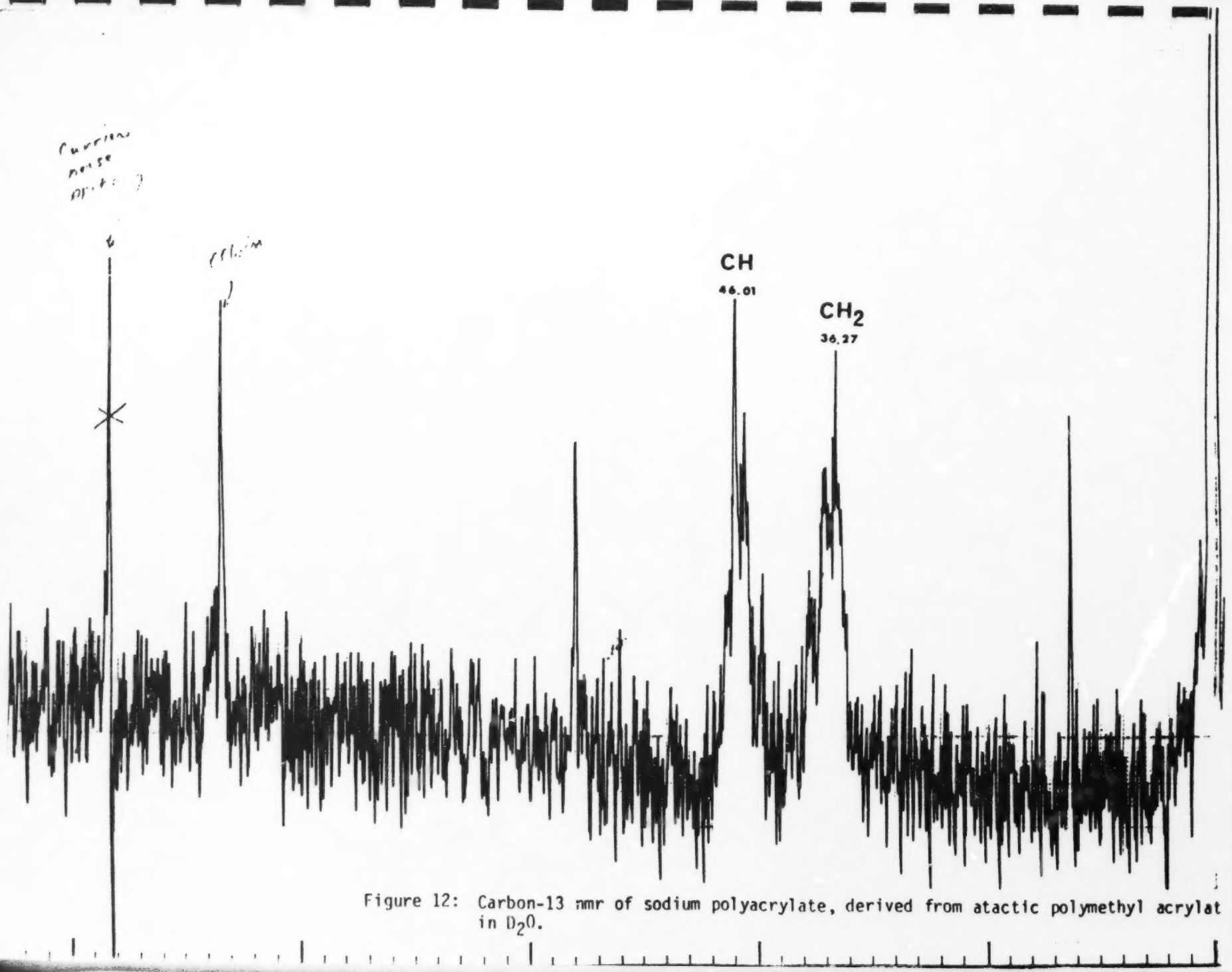


Figure 12: Carbon-13 nmr of sodium polyacrylate, derived from atactic polymethyl acrylat in D_2O.

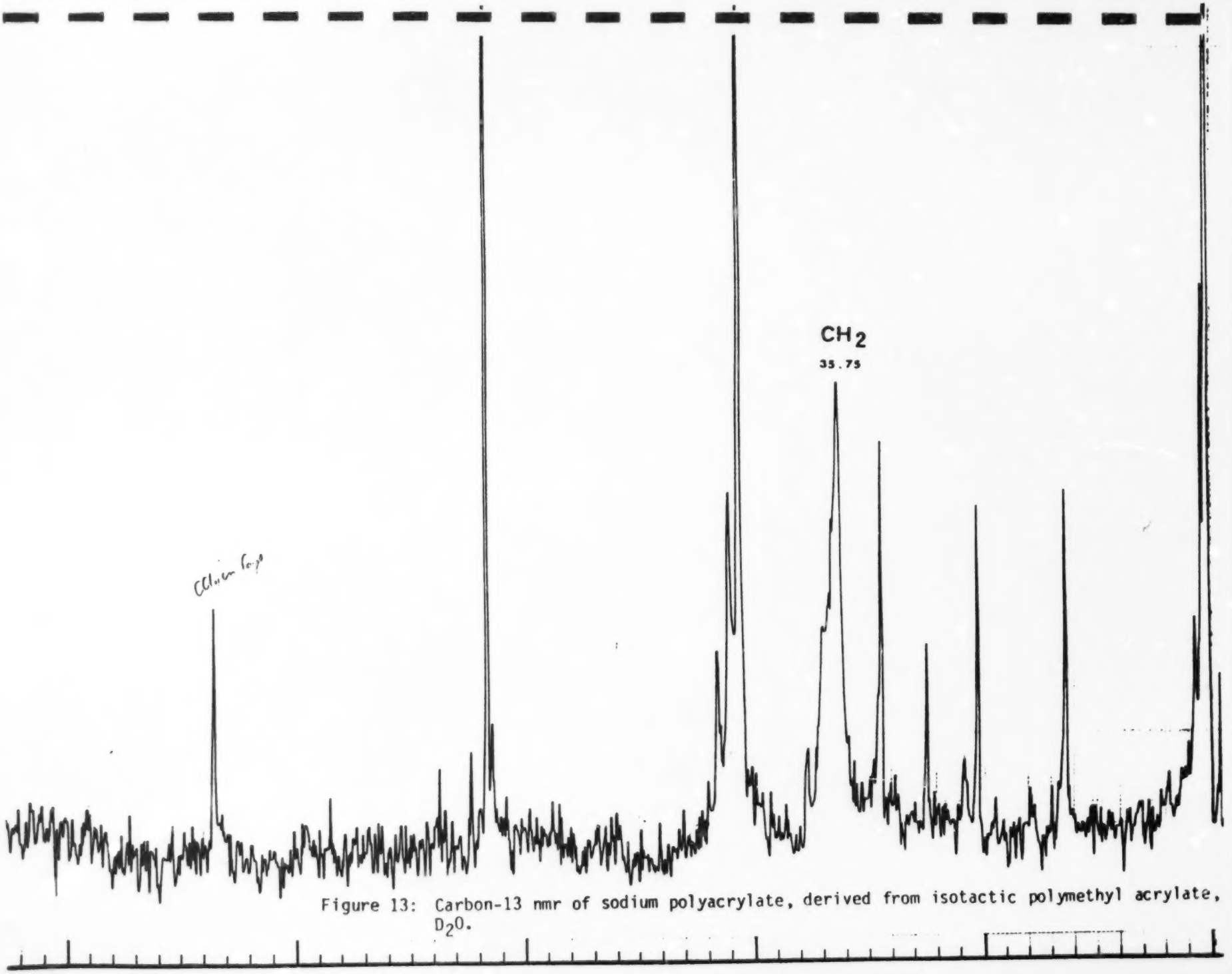


Figure 13: Carbon-13 nmr of sodium polyacrylate, derived from isotactic polymethyl acrylate, D_2O.

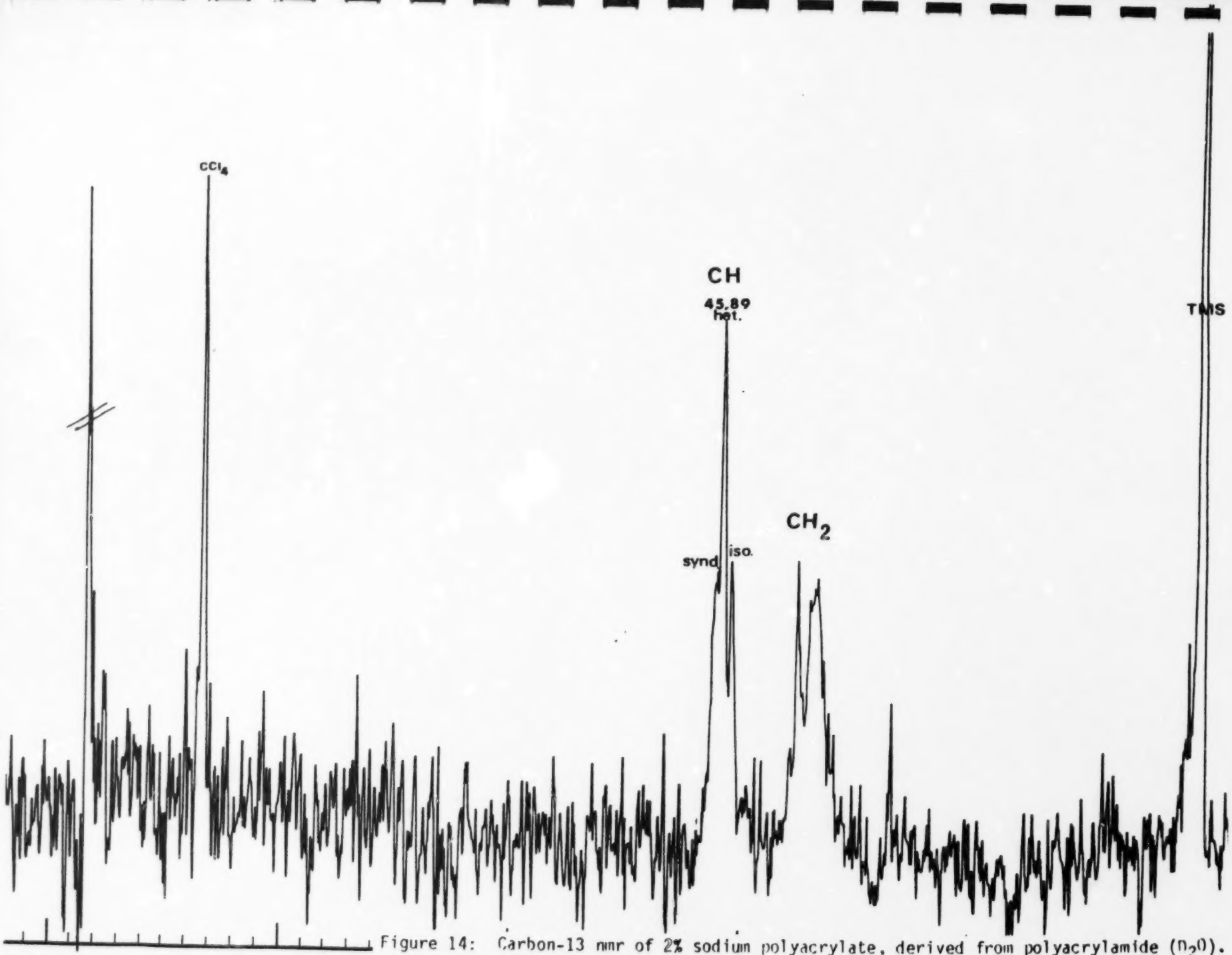


Figure 14: Carbon-13 nmr of 2% sodium polyacrylate, derived from polyacrylamide (D_2O).

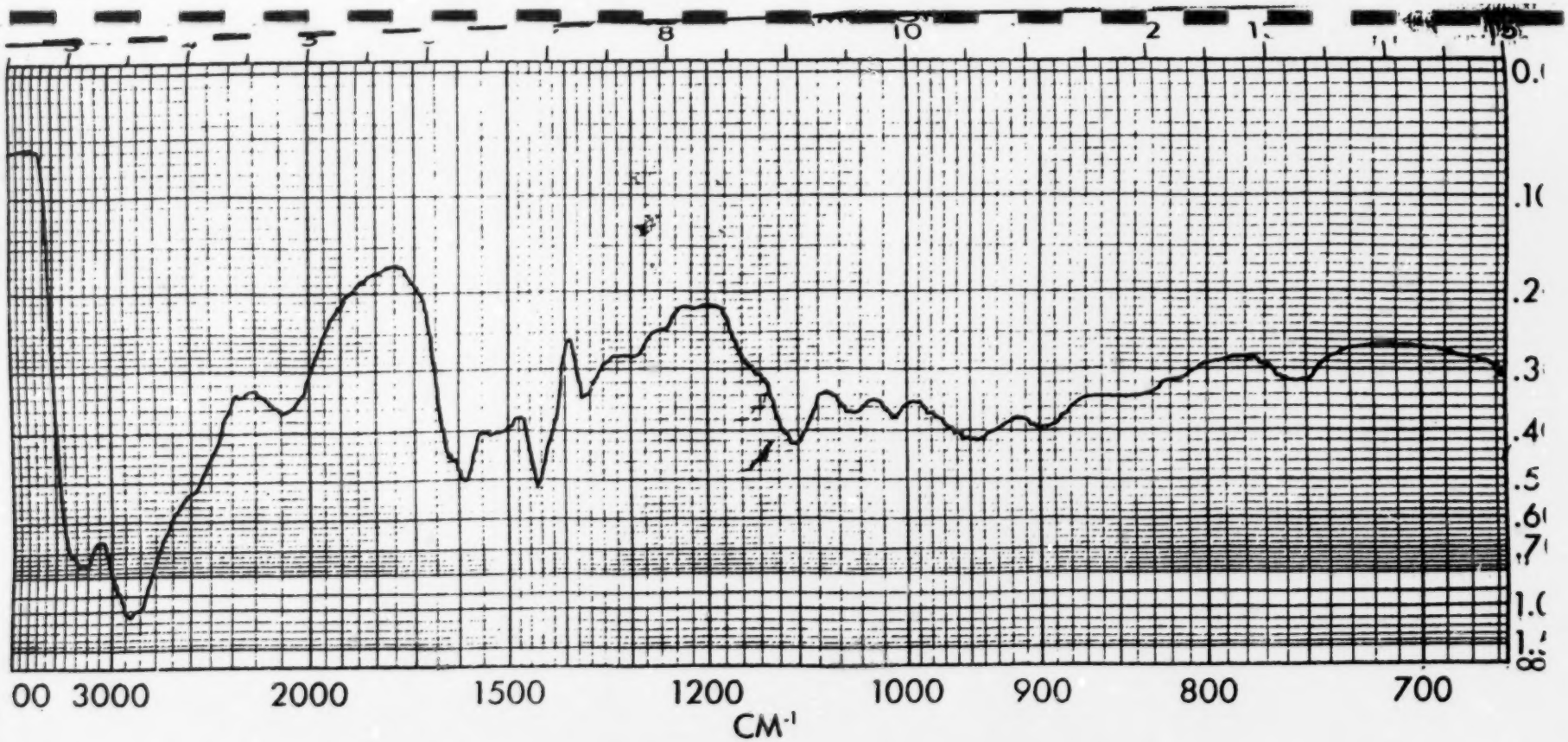


Figure 15: Synthetic polyamine (film).

3400 - 3200 cm^{-1}; N-H

2900 cm^{-1}; C-H

2100 cm^{-1}; N-H

1600 cm^{-1}; N-H

1450 cm^{-1}; C-H

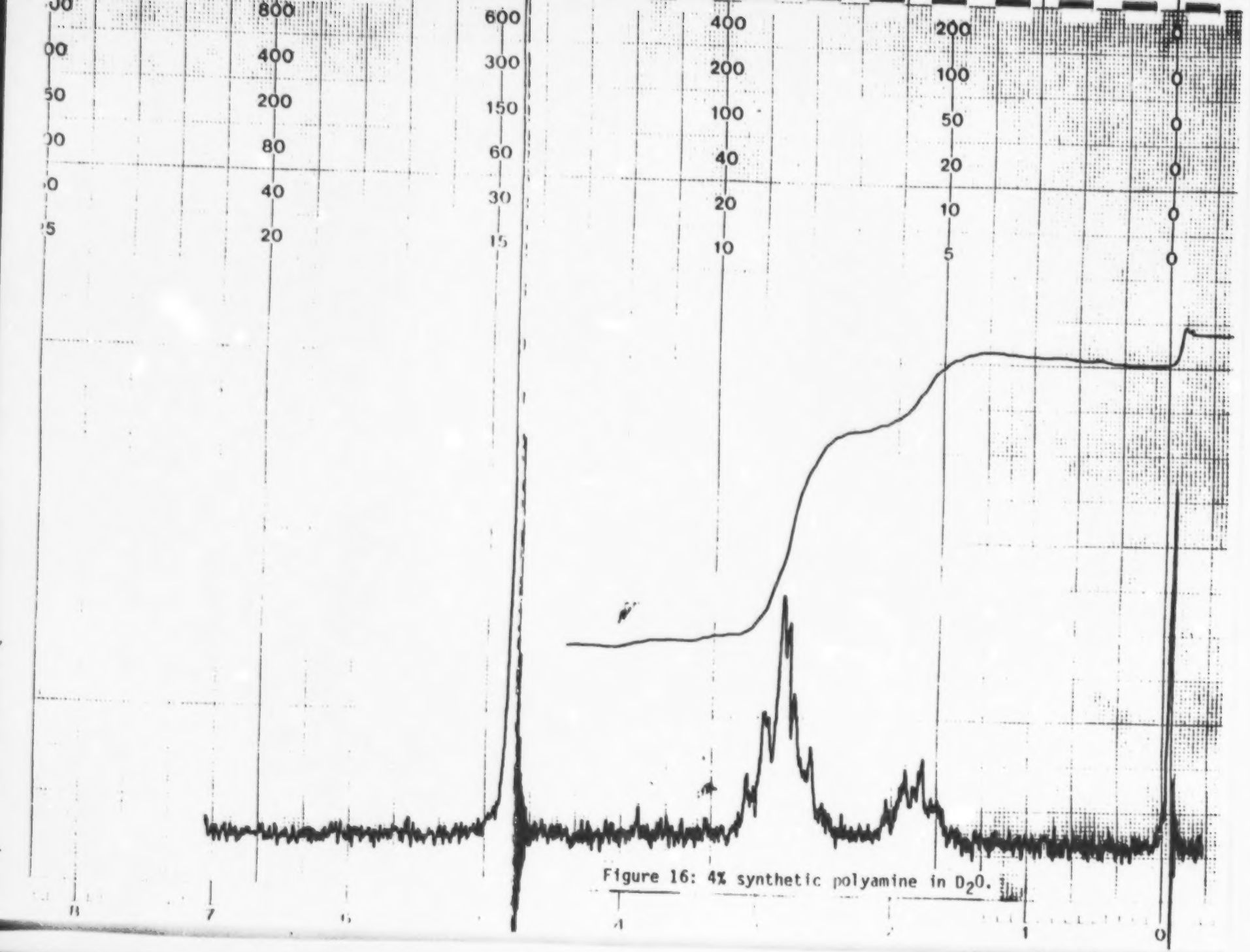


Figure 16: 4% synthetic polyamine in D_2O.

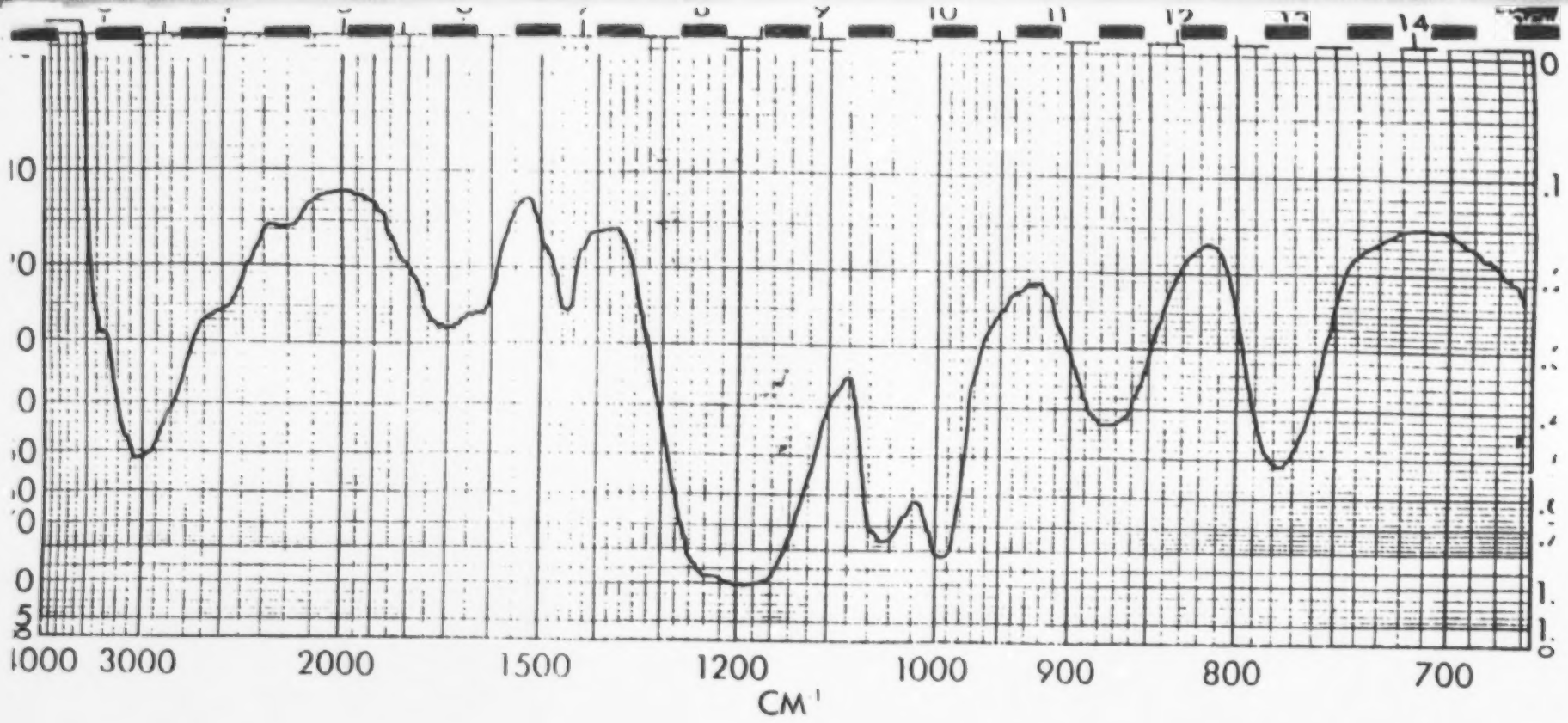


Figure 17: Quaternized synthetic polyamine (film)

3400 cm^{-1}; H_2O, NH

1700 cm^{-1}; N-H (unreacted)

1200 cm^{-1}; sulphate

3300 - 2600 cm^{-1}; C-H

1450 cm^{-1}; C-H

1000 cm^{-1}; methyl sulphate?

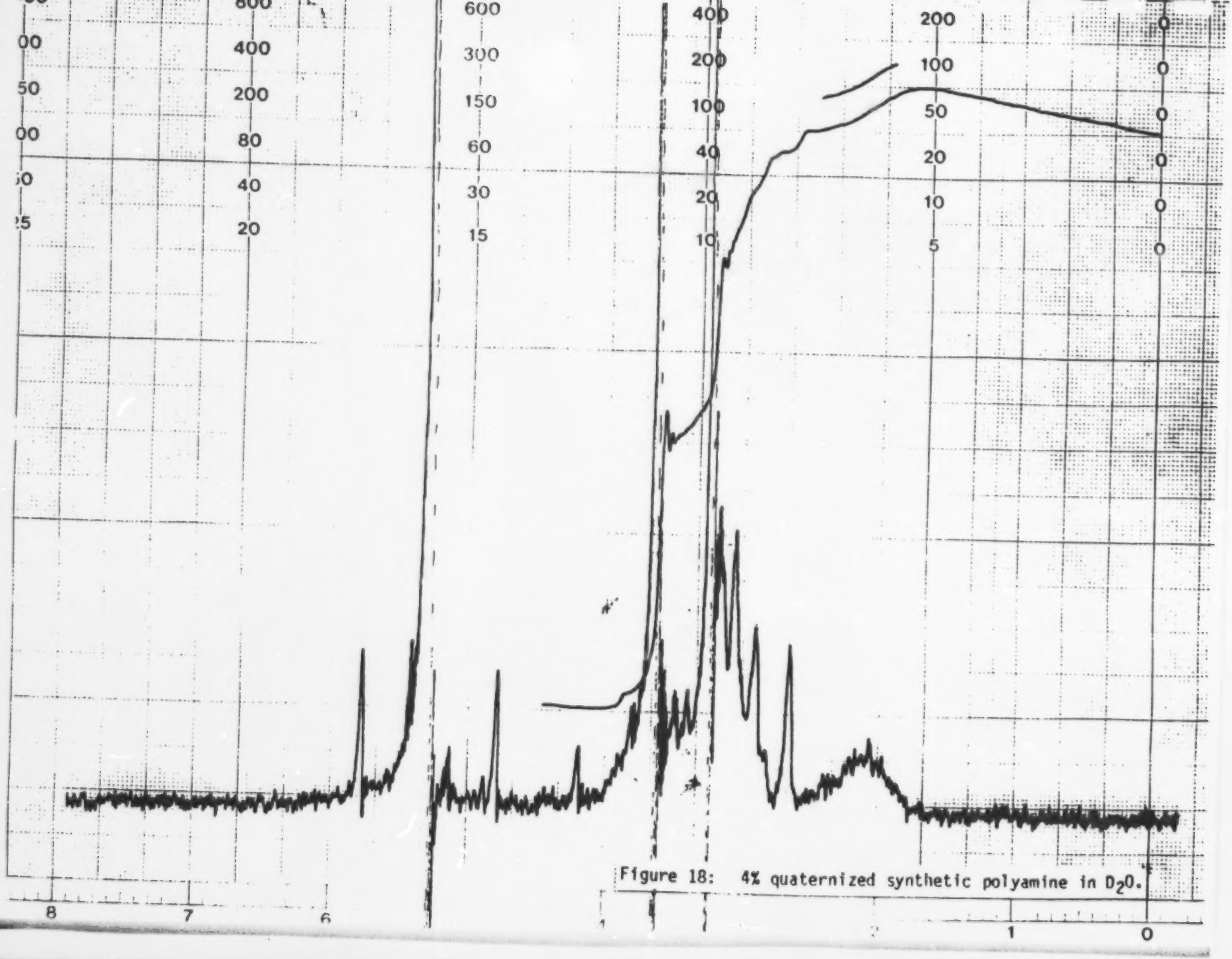


Figure 18: 4% quaternized synthetic polyamine in D_2O.